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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

SOME SALTS OF IMIDOSULFAMIDE. II.

L. M. Volshtein and M. M. Slutskaya

The barium, silver, and copper salts of imidosulfamide $(NH_2SO_2)_2NH$(HIm) were described in the preceding report [1]. We synthesized and investigated several other salts of imidosulfamide. It was found that the behavior of the acid radical of imidosulfamide, $(NH_2SO_2)_2N^-$(Im), entering into the composition of the salts depends essentially on the nature of the associated cation. This circumstance led us to continue the study of imidosulfamide salts. In this report the nickel and zinc salts are described, and additional data on the copper salt are also given.

Nickel Imidosulfamide

This salt was obtained from $BaIm_2$ and $NiSO_4$, taken in equimolar quantities; portions of analyzed $BaIm_2$ (1-2 g) were dissolved in 3-6 ml of water, and the calculated volume of titrated $NiSO_4$ solution was added. The $BaSO_4$ precipitate was filtered off, and the filtrate was evaporated in vacuo at room temperature or at 60-70°. When a considerable part of the salt had crystallized, the evaporation was stopped. The green crystals of the nickel salt were filtered and dried to constant weight at 90°. The salt was prepared several times, and analyses confirmed the constancy of its composition.

Found %: Ni 13.16, 13.09; N 18.51, 18.44; S 28.55, 28.50. $NiN_6H_8O_8S_4 \cdot 2H_2O$. Calculated %: Ni 13.25; N 18.97; S 28.94. $NiN_6H_8O_8S_4 \cdot 2.5H_2O$. Calculated %: Ni 12.98; N 18.59; S 28.37.

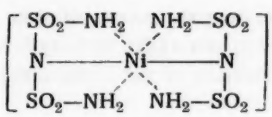
From the average content of nickel (13.06%), nitrogen (18.48%), and sulfur (28.52%), the ratios N/Ni = 5.93 and S/Ni = 3.99 were found. The theoretical ratios for the nickel salt of imidosulfamide are N/Ni = 6 and S/Ni = = 4. The determined percentage composition of Ni, N, and S is less than that corresponding to the anhydrous salt and close to that of the dihydrate (although it is even closer to that of the crystal hydrate $NiIm_2 \cdot 2.5H_2O$).

An attempt at dehydration of the salt in vacuo and with heating did not yield any positive results. At 120° the salt does not lose water, and at 140° it begins to melt and to decompose. Dehydration of the salt was accomplished by shaking it with alcohol. About 1 g of the salt was dropped into 100 ml of 96° ethyl alcohol and shaken for a long time (about 20 hours). The salt was filtered off by suction, dried at 90° to constant weight, and analyzed.

Found %: Ni 14.36, 14.44; N 20.49, 20.46; S 31.50, 31.33. $NiN_6H_8O_8S_4$. Calculated %: Ni 14.42; N 20.65; S 31.50.

The anhydrous salt differs in external form from the crystal hydrate. It, too, is green, but has a bluish tinge. Both the anhydrous salt and the crystal hydrate are readily soluble in water or alcohol–water mixtures, but are practically insoluble in 96° alcohol.

On dissolving in water, the anhydrous salt is not converted to the crystal hydrate. We prepared a 0.1 M solution of the anhydrous salt. The solution stood a long time (several weeks), and then was evaporated at 70° until crystals formed. The crystals were dried at 90° and analyzed. Found: 14.40 and 14.41% Ni. Calculated: 14.42% Ni for the anhydrous salt, 13.25% Ni for the dihydrate. Thus, dehydration accomplished by shaking with alcohol proved irreversible. Similar phenomena are seldom observed, and we conceived the hypothesis that the anhydrous salt is an internal-complex compound having the structure.



However, measurement of the electrical conductivity of the 0.1 M solution revealed that the molar conductivity of the anhydrous salt (60 $ohm^{-1}cm^2$ at 25°) is only slightly less than that of the crystal hydrate (70 $ohm^{-1}cm^2$ at the same concentration). Note that in 0.1 M solutions of all studied imidosulfamide salts ($BaIm_2$, $CuIm_2$, $NiIm_2$, and $ZnIm_2$), the molar conductivity is appreciably lower than in 0.1 M solutions of ordinary triionic electrolytes [1]. The molar conductivity of dilute solutions does not differ from the usual values; for the anhydrous nickel salt and its crystal hydrate, values found in 0.001 M solutions were 225 and 235 $ohm^{-1}cm^2$ at 25°.

Zinc Imidosulfamide

In order to obtain $ZnIm_2$, we mixed together concentrated solutions of the salts $BaIm_2$ and $ZnSO_4$, taken in equimolar quantities. The $BaSO_4$ precipitate was filtered off, and the filtrate was evaporated in vacuo to an oily consistency. After standing several days, the oily liquid crystallized. The crystals were filtered, dried to constant weight at 90°, and analyzed. The salt was prepared several times, and its composition proved constant. From the average percentage composition of zinc (14.61%), sulfur (28.59%), and nitrogen (18.68%), the ratios S/ Zn = 3.99 and N/ Zn = 5.97 were found. The theoretical ratios for the zinc salt of imidosulfamide are S/ Zn = 4 and N/ Zn = = 6. The determined percentage composition of Zn, S, and N corresponds to that of the dihydrate.

Found %: Zn 14.69, 14.62; S 28.57, 28.62; N 18.67, 18.70. $ZnN_6H_8O_8S_4 \cdot 2H_2O$. Calculated %: Zn 14.54; S 28.51; N 18.69.

The salt is white with a faint yellowish tinge; it is readily soluble in water and very slightly soluble in alcohol. It does not lose water in crystallization at 110°. The melting point could not be determined because the salt began to decompose at 120°. An attempt at dehydration of the salt by shaking the crystal hydrate with alcohol did not yield positive results (see below). The molar conductivity of a 0.001 M solution was found to be 232 $ohm^{-1}cm^2$ at 25°; as the salt concentration increased, the molar conductivity decreased considerably. In a 0.1 M solution it was 95 $ohm^{-1}cm^2$.

Shaking of the Salts With Alcohol

It is stated above that the crystal hydrate of the nickel salt is dehydrated on shaking with alcohol. A substantially different result is obtained on shaking the crystal hydrates of the copper and zinc salts with alcohol. Cupric imidosulfamide monohydrate, described earlier [1], was shaken a long time (20 hours) with alcohol. For 1-1.2 g of $CuIm_2 \cdot H_2O$, 120-140 ml of 96° ethyl alcohol was taken. The precipitate was filtered off and dried to constant weight at 90°. The product thus obtained differed from the original salt in external form and, as analyses revealed, contained nearly 25% copper, although anhydrous $CuIm_2$ contains 15.43% Cu. Obviously, the $CuIm_2$ had decomposed. The N/ Cu and S/ Cu ratios found for the obtained product proved to be near 2, a value corresponding to cupric sulfamate.

Found %: Cu 24.77, 24.59, 24.85; S 25.15, 25.20; N 10.80, 10.76. $Cu(OSO_2NH_2)_2$. Calculated %: Cu 24.86; S 25.07; N 10.95.

Thus the reaction product proved to be anhydrous cupric sulfamate. We dissolved it in water, evaporated the solution in vacuo at room temperature, and analyzed the air-dried product. The Cu content of the latter was found to be 22.15%, which is near that of $Cu(OSO_2NH_2)_2 \cdot 2H_2O$ (calculated Cu content, 21.78%); according to literature data, cupric sulfamate crystallized as the dihydrate. The course of the reaction may be as follows:

$$Cu\left(N\begin{matrix}SO_2-NH_2\\ \\ SO_2-NH_2\end{matrix}\right)_2 + 2H_2O \rightarrow Cu(OSO_2NH_2)_2 + 2NH_2SO_2NH_2$$

After filtering off the cupric sulfamate, we evaporated the alcholic solution. The solid residue was recrystallized from ethyl acetate. The crystal form and melting point (91.2°) indicated that sulfamide (m.p. 92-93° according to literature data) had been formed in the reaction.

The acid residue of imidosulfamide in neutral aqueous solutions is stable at room temperature, but rapidly hydrolyzes at the boiling point or in an acid medium [2]. Hydrolysis in an alcoholic medium containing little water is apparently promoted by the high solubility of one of the reaction products (sulfamide) in alcohol and the

insolubility of the other product (cupric sulfamate) in that medium.

We shook the crystal hydrate of zinc imidosulfamide with alcohol for about 21 hours (taking 150 ml of 96° alcohol for 1.2 g of $ZnIm_2 \cdot 2H_2O$). In this case, a more drastic cleavage occurred than in the case of the copper salt. The filtered-off precipitate proved to be zinc sulfate mixed with a small amount of ammonium sulfate. Analysis showed that it contained about 36% Zn, 18.6% S, and 2.7 % N. The Zn and S content of the precipitate approximates that of the monohydrate $ZnSO_4 \cdot H_2O$ (36.43% Zn and 17.86% S). The small amount of nitrogen [we note that the initial $ZnIm_2 \cdot 2H_2O$ contains 18.69% N, and that the zinc sulfamate $Zn(OSO_2NH_2)_2$ contains 10.9% N] is due to the admixture of ammonium salt. The conversion taking place is described by the equation.

$$Zn\left(N\begin{matrix}SO_2-NH_2\\SO_2-NH_2\end{matrix}\right)_2 + 4H_2O \rightarrow ZnSO_4 + (NH_4)_2SO_4 + 2NH_2SO_2NH_2$$

We synthesized zinc sulfamate (from $ZnCO_3$ and sulfamic acid) in order to determine whether it is transformed when shaken with alcohol. A suspension of 0.8 g of zinc sulfamate (dried at 90°) in 100 ml of alcohol was shaken for about 20 hours. Analysis showed that the zinc sulfamate had been converted to $ZnSO_4 \cdot H_2O$ (found: 36.1% Zn) mixed with a little $(NH_4)_2SO_4$. The stability of cupric sulfamate when it is shaken with alcohol and the conversion of zinc sulfamate to the sulfate under the same conditions are consistent with the composition of the final products obtained when cupric and zinc imidosulfamides are shaken with alcohol. Thus the behavior of each of the three salts under investigation is essentially different, depending on the nature of the cation. It would be of interest to prepare salts with other cations (Co^{++}, Mn^{++}) and to determine their behavior under analogous conditions.

SUMMARY

1. Nickel imidosulfamide (the anhydrous salt $Ni[N(SO_2NH_2)_2]_2$ and the dihydrate) has been synthesized.

2. Zinc imidosulfamide $Zn[N(SO_2NH_2)_2]_2 \cdot 2H_2O$ has been synthesized.

3. It has been shown that on prolonged shaking with alcohol cupric imidosulfamide is converted to the sulfamate, and zinc imidosulfamide is changed to the sulfate. The crystal hydrate of nickel imidosulfamide is only dehydrated by this treatment.

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INVESTIGATION OF PHASE EQUILIBRIA IN THE PYRAMIDON–DIETHYLAMINE–WATER SYSTEM

I. L. Krupatkin and I. A. Todorov

It was shown earlier that in the pyramidon–salicylic acid–water system the compound of its predominant binary system has homogenizing properties. For this reason the stratification region of the ternary system was divided into two parts [1]. The homogenizing properties of compounds formed in systems have been investigated very little; nevertheless, they may be of practical importance in the choice of mixed solvents. In this work the study of the homogenizing properties of such compounds is continued. The pyramidon–diethylamine–water system was chosed for investigation. In the predominant pyramidon–diethylamine system of the latter, the presence of a dissociated compound was established. The presence of this compound, together with that of two stratified, subordinate binary systems, gave rise to the hypothesis that two separate stratification regions occur in the chosen ternary system. It is of interest to obtain an equilibrium diagram of the conjectured type since only isolated cases of ternary systems with two separate stratification regions are known in the literature [1, 2].

EXPERIMENTAL

The following substances were used in the work: pharmacopoeia-grade pyramidon (m.p. 108°), distilled diethylamine (b.p. 56°), and redistilled water. The investigation of stratification in the system was conducted by the method of V. F. Alekseev [3]; the melting-point investigation was carried out in ampules by the visual method, with an internal primer [4]. Ampules, containing the volatile diethylamine exploded above 150°; this fixed the upper temperature limit in the investigation. Those binary systems of the ternary one under study, which are formed with water, are discribed in the literature. The pyramidon–water system has been studied with regard to stratification and fusibility [1].

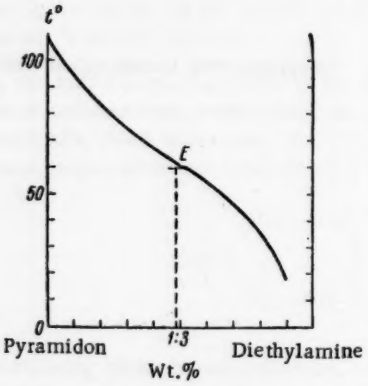

Fig. 1. Fusibility diagram of the pyramidon–diethylamine system.

The phase diagram of the system has a closed stratification curve with two critical points, the upper located in the region of stable equilibrium and the lower situated below the crystallization curve of pyramidon. The diethylamine–water system has been investigated with regard to stratification [5]. The stratification curve has a lower critical point. The investigation of the predominant pyramidon–diethylamine system is described in the present work.

The pyramidon–diethylamine (P – D) system was investigated with regard to fusibility. The numerical data obtained are given in Table 1, and the fusibility diagram is shown in Fig. 1. As Fig. 1 indicates, there is one incongruently melting compound in the system; it contains 48.67% diethylamine and 51.33% pyramidon (PD_3). The observed transition point E corresponds to a temperature of 60.5° and a pyramidon content of 49.7%.

The pyramidon–diethylamine–water (P – D – W) system was investigated with regard to stratification and, in part, fusibility. For this purpose polythermal sections through the temperature-concentration prism of the system,

extending from the water edge to the boundary of the pyramidon–diethylamine system were taken. Seven sections containing 0.6, 1.0, 10.0, 20.0, 30.0, 35.0 and 99.7% diethylamine were studied. Numerical data on the

TABLE 1

Equilibrium in the Pyramidon–Diethylamine System

Diethylamine content (Wt. %)	Crystallization temperature	Diethylamine content (Wt. %)	Crystallization temperature	Diethylamine content (Wt. %)	Crystallization temperature
5.00	101.5°	46.50	63.5°	55.00	58.0°
11.74	91.5	48.14	62.5	60.00	54.0
15.00	88.5	49.00	61.5	65.00	50.0
20.00	84.0	49.50	61.0	70.30	45.0
25.00	79.5	50.00	60.5	75.00	41.0
30.00	75.5	50.48	60.5	80.00	36.0
35.00	71.0	51.00	60.5	85.15	28.0
40.00	68.0	52.00	60.0	90.00	18.0
45.00	64.5	53.00	59.0		

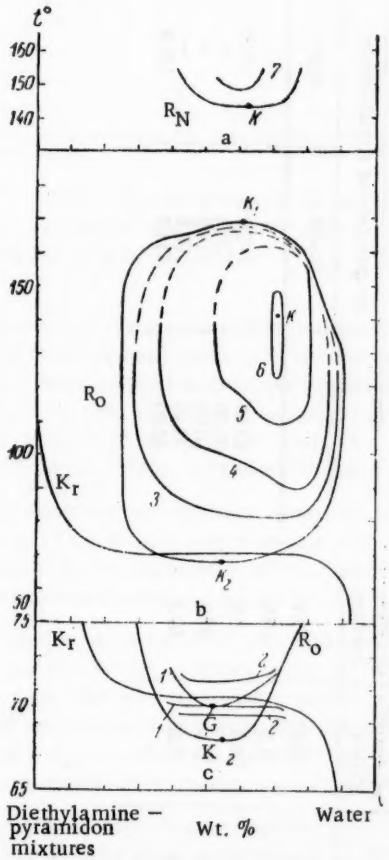

Fig. 2. Polytherms of the ternary system, pyramidon–diethylamine–water.
a) Adjoining the boundary of the diethylamine–water system, b) adjoining the boundary of the pyramidon–water system; c) the lower portion of the latter, drawn to a large scale along the temperature axis. Explanation in text.

sections are given in Table 2, and the stratification polytherms are given in Fig. 2. The dashed lines indicate portions of the polytherms, which were not studied owing to explosions of the ampules. Stratification curves of the binary systems pyramidon–water (R_0) and diethylamine–water (R_N) are also given in Fig. 2. In the concentration interval from 35 to 99% diethylamine stratification does not occur in the ternary system. In this interval is located that cross section of the temperature-concentration prism of the ternary system, which intersects the pyramidon–diethylamine system at the composition of the compound PD_3, the latter being present in these systems in the liquid phase, as will be shown below. The specified cross section is not strictly quasi-binary. Nevertheless, since there are two separate regions of stratification in the ternary system under study, the cross section will divide the entire ternary system into two ternary systems: water–diethylamine–PD_3 and water–PD_3–pyramidon. The polytherm of the water–diethylamine–PD_3 system is shown in Fig. 2a. Polytherms of the water–PD_3–pyramidon system are shown in Fig. 2b; the lower part of the latter, drawn to a large scale, appears in Fig. 2c. In the two ternary systems formed by the crosss section, the two-phase binary systems, pyramidon–water and diethylamine–water, are homogenized by PD_3. The division of the stratification region of the entire ternary system into two separate parts is due to its strong homogenizing properties. The homogenizing properties of the compound PD_3, in turn, are connected with its strong dissociation; its unlimited solubility in water is due to the latter.

As Fig. 2a indicates, the polytherm of the water–diethylamine–PD_3 system has a lower critical solution temperature. A total pyramidon content of

TABLE 2

Equilibrium in the Pyramidon–Diethylamine–Water System

Section 1: 0.6% diethylamine, 99.4% pyramidon

Water (wt.%)	temperature of stratification	temperature of crystallization
40.00	72.0°	70.0°
50.00	70.0	70.0
55.00	70.0	70.0
60.00	70.5	70.0
70.00	71.5	70.0

Section 2: 1.0% diethylamine, 99.0% pyramidon

water (Wt.%)	temperature of stratification	temperature of crystallization
42.86	72.0°	69.5°
44.44	71.5	69.5
51.45	71.5	69.5
57.34	71.5	69.5
70.00	72.0	69.5

Section 3: 10.0% diethylamine, 90.0% pyramidon

water (wt.%)	temperature of stratification
28.50	114.0°
29.00	105.0
32.04	98.5
35.00	93.5
43.03	86.0
50.00	84.0
60.00	82.0
70.00	81.5
80.00	83.5
86.00	94.0
87.07	97.0
88.25	104.5
88.50	110.0

Section 4: 20% diethylamine, 80.0% pyramidon

water (wt.%)	temperature of stratification
36.50	128.0°
37.12	120.0
38.55	113.0
40.41	110.5
44.75	103.5
50.00	101.5
60.00	98.0
70.00	92.5
80.39	91.0
82.00	97.0
85.00	101.5
86.04	122.0

Section 5: 30.0% diethylamine, 70.0% pyramidon

water (wt.%)	temperature of stratification	
	lower	upper
52.00	137.0°	140.0°
55.00	120.5	—
60.00	118.0	—
70.15	109.0	—
80.00	114.5	155.0

Section 6: 35.0% diethylamine, 65.0% pyramidon

water (wt.%)	temperature of stratification	
	lower	upper
69.61	127.0°	145.0°
70.00	122.0	149.0
72.00	132.0	144.0

Section 7: 99.7% diethylamine, 0.3% pyramidon

water (wt.%)	temperature of stratification
55.00	150.0°
57.00	149.0
62.50	149.0
65.00	151.0

0.3 % (section 7) raises the lower critical point of the binary system, diethylamine–water, 5.5°. In accordance with this, the region bounded by the solubility curves of the liquid phases is sharply contracted. Hence the volume of the stratification region adjoining the boundary of the diethylamine–water system is very small. As Fig. 2b shows, the polytherms of the water–PD_3–pyramidon system are closed curves which contract concentrially as the diethylamine content of the mixtures increases. Ultimately they are transformed into the triple point of solubility change, K [1]. The temperature of this triple point is 141°; the corresponding composition is 19% pyramidon, 11% diethylamine, and 70% water.

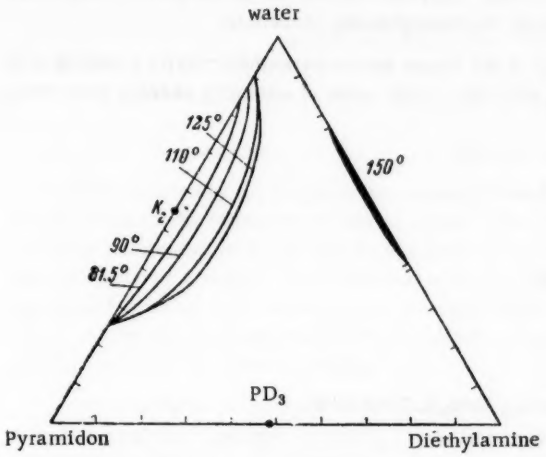

Fig. 3. Stratification isotherms of the ternary system, pyramidon–diethylamine–water. Explanation in text.

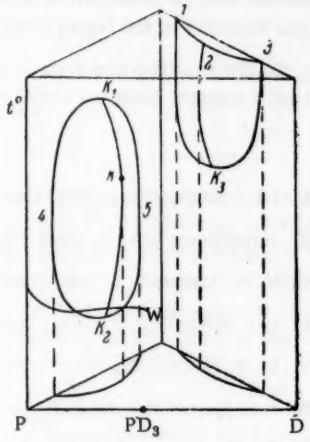

Fig. 4. General form of the temperature-concentration prism of the ternary system, pyramidon (P) – diethylamine (D) – water (W). Explanation in text.

That part of the diagram of the ternary system, pyramidon–diethylamine–water, which is located near the pyramidon–water system boundary, is of interest since, as the temperature rises, a transition from a metastable equilibrium between the liquid phases to a stable one occurs. It was shown [6] that such transitions can only take place through sections with contact and contact points on the stratification and fusibility curves. As Fig. 2c shows, Section 1 (0.6% diethylamine) is a section with contact. The contact point G therein corresponds to the composition 47.2% pyramidon, 0.3% diethylamine, 52.5% water and the temperature 70°.

The described homogenizing properties of the compound PD_3 indicate the presence of this compound in the liquid phase of the ternary system and its predominant binary system. This confirms the possibility of detecting the compound in the liquid phase of the system by its homogenizing properties [1]. In the given case the finding of this same compound on the fusibility diagram of the predominant system, as well, is even more reasonable.

Solubility isotherms of the liquid phases of the pyramidon–diethylamine–water system were plotted from the obtained polytherms, as shown in Fig. 3. For the volume of the stratification region adjoining the pyramidon–water system, four isotherms were plotted at 81.5, 90, 110 and 125°. Owing to the strong homogenization, the volume of the stratification region adjoining the boundary of the diethylamine–water system is very small. For this reason a single isotherm is plotted at 150° for the given volume in Fig. 3; it is shown in the form of a thickening of the diethylamine–water system boundary.

The general form of the temperature-concentration prism of the pyramidon–diethylamine–water system is shown in Fig. 4, in which the letters in the corners of the prism are the initial letters of the components. As is apparent from Fig. 4, the stratification surface $K_1 4 K_2 5 K$ is a closed surface and therefore is not connected to the second stratification surface $123K_3$. The two stratification surfaces have the lower critical points K_2 and K_3. The ternary system, pyramidon–diethylamine–water, has a new type of phase diagram in which the stratification surface of the ternary system is divided into two surfaces, each of which has a lower critical point.

SUMMARY

1. The binary system, pyramidon–diethylamine, has been studied with regard to fusibility. A single, incongruently melting compound was discovered therein. The observed transition point corresponds to a diethylamine content of 49.7% and a temperature of 60.5°.

2. The ternary system, pyramidon–diethylamine–water, has been studied with regard to stratification, and, in part, to fusibility. It has been shown that the phase diagram of the ternary system has two separate stratification surfaces with lower critical points. It has been proved that the occurrence of this type of equilibrium between liquid phases is due to the strong homogenizing properties of the compound of the predominant binary system, which are connected with its dissociation in the third component – water. This same compound of the predominant binary system was detected in the liquid phase of the ternary system by its homogenizing properties.

3. On the stratification surface adjoining the boundary of the binary system pyramidon–water a section with contact and a contact point for lower critical temperatures, and also a triple point of solubility change, were found.

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DIPOLE MOMENTS OF COMPLEX COMPOUNDS OF ZIRCONIUM TETRACHLORIDE WITH ESTERS OF MONOBASIC ACIDS. XII

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The reaction of tin and titanium tetrachlorides with various nitrogen- and oxygen-containing organic compounds leads to the formation of complex molecules with high dipole moments [1, 2, 3]. The high polarity of the complex compounds of $SnCl_4$ and $TiCl_4$ cannot be explained by polarization interaction alone; rather, it indicates the formation of a strongly polarized dative bond. The pronounced capacity of tin and titanium tetrachlorides for complex formation with various types of organic compounds containing nitrogen, oxygen, and sulfur is obviously explained by the ease with which the incomplete d-electron levels of the central atom are filled by the labile electron pairs of the donor atom [4].

The results of determination of the dipole moments of complex compounds formed by zirconium tetrachloride with ethyl and isopropyl formates, ethyl, isopropyl, isobutyl, and benzyl acetates, and ethyl butyrate are reported in the present work. According to Sidgwick [5], zirconium can form complex compounds with the coordination numbers 5, 6, 7 and 8. In all these compounds the zirconium atom acts as an electron acceptor. Blumenthal [6] considers that all reactions of quadrivalent zirconium may be referred to two principal types:* reactions in which only normal valence bonds participate

$$ZrX_4 + 4Y \rightleftharpoons ZrY_4 + 4X$$

and reactions in which coordinate-covalent bonds take part

$$ZrY_4 + pA \rightleftharpoons [ZrY_4 \cdot pA]$$

In the given equations X and Y represent univalent elements or groups or the corresponding equivalents of multivalent atoms; A is a molecule having paired, labile electrons which takes part in the formation of dative bonds; p is an integer not exceeding eight. As the experimental data show, p rarely exceeds four; i.e., in complex compounds of the type $ZrY_4 \cdot pA$ the coordination number of zirconium is usually six.

Zirconium tetrachloride, like tin and titanium tetrachlorides, exhibits a strong tendency toward complex formation with various nitrogen- and oxygen-containing organic compounds. Thus addition compounds of esters and $ZrCl_4$ were obtained by Moore and Tyree, Rosenheim, and others [7-10]. These compounds are white, crystalline substances, stable in dry air; in the presence of water they readily dissociate, giving zirconium chloride and the appropriate ester. The addition reaction of the ester and $ZrCl_4$ is accompanied by an appreciable heat effect. For instance, in the formation of the complex compound $ZrCl_4 \cdot C_6H_4(COOC_2H_5)_2$ 18.2 kcal/mole of heat is evolved. On the basis of their investigations Moore and Tyree conclude that in all the complex compounds obtained by them, the coordination number is six, which accords with our investigations.

Preparation of Materials and Experimental Procedure

The method of measuring the dielectric constant, refractive index, and density and that of determining the properties of the benzene used for preparation of solutions were given earlier [3, 11]. The esters were washed with sodium carbonate solution, dried with anhydrous calcium chloride, and subjected to fractional distillation. For

* The given reaction schemes may be complicated, for instance, by partial displacement of X by Y, etc.

this work fraction boiling in the following ranges were used:

	Boiling Point	d_4^{20}	n_D^{20}
$HCOOC_2H_5$	54.2— 54.4°	0.9071	1.3596
iso-$HCOOC_5H_7$	70.8— 71.1	0.8732	1.3702
$CH_3COOC_2H_5$	77.1— 77.4	0.9004	1.3725
$CH_3COOC_3H_7$	101.6—102.0	0.8859	1.3842
iso-$CH_3COOC_4H_9$	112.6—113.1	0.8706	1.3886
$CH_3COOCH_2C_6H_5$ . . .	213.5—214.0	1.0517	1.5238
$C_3H_7COOC_2H_5$	120.4—121.0	0.8780	1.3930

"Pure"-grade zirconium tetrachloride was purified by vacuum sublimation, the first portion of the sublimate, which was contaminated with volatile admixtures, being discarded. The perfectly white zirconium tetrachloride obtained after sublimation was analyzed for its chlorine content. The latter differed from the theoretical value not more than 0.05%. All purified materials were stored in sealed ampules. We prepared benzene solutions of the complex compounds under study, starting with stoichiometric quantities of zirconium tetrachloride and the appropriate ester, in a special chamber in a current of dry air. During the measurements, all possible precautions against the penetration of moisture were taken.

The dielectric constant, refractive index, and density were determined at 20° ± 0.1. The polarization (P_2) of each dissolved complex compound was found from the concentration dependence of its dielectric constant and density in benzene, and was extrapolated to infinite dilution (P_∞). Dipole moments were calculated by means of the formula $\mu = 0.012813\sqrt{(P_\infty - P_D)T}$. The electronic polarization was equated with the molar refraction, and the atomic polarization was taken to be 15% of the latter [12].

Experimental Results and Discussion Thereof

In Table 1 and 2 are given the results of dielectric-constant (ϵ) and density (d) measurements on the complex compounds of zirconium tetrachloride with ethyl and isoamyl formates, and also the corresponding calculated polarization (P_2) values, as functions of the mole fraction of the complex in benzene.

TABLE 1

Complex $ZrCl_4 \cdot 2HCOOC_2H_5$ in Benzene

P_∞ = 1285 cc, R = 73.45 cc

C (mole fraction)	ϵ	d	P_2
0.00248	2.504	0.8831	1246
0.00349	2.584	0.8849	1224
0.00586	2.798	0.8896	1207
0.00868	3.035	0.8950	1147
0.01310	3.397	0.9036	1066

TABLE 2

Complex $ZrCl_4 \cdot 2HCOOC_5H_7$ in Benzene

P_∞ = 1340 cc, R = 83.16 cc

C (mole fraction)	ϵ	d	P_2
0.00322	2.585	0.8844	1335
0.00372	2.632	0.8853	1328
0.00500	2.766	0.8880	1336
0.00642	2.895	0.8905	1296
0.00962	3.158	0.8965	1191
0.01420	3.381	0.9046	1001

For the complex compound $ZrCl_4 \cdot 2HCOOC_2H_5$ the polarization, extrapolated to infinite dilution (P_∞), is 1285 cc, and the deformation polarization, which is equal to the sum of the electronic and atomic polarizations, is 84.46 cc. The dipole moment, calculated by means of the Debye formula given above, is 7.63 D. Corresponding values for the complex $ZrCl_4 \cdot 2HCOOC_5H_7$ are 1340 cc, 95.46 cc, and 7.76 D.

The results of dielectric constant measurements and the calculated polarization values for benzene solutions of the complex compounds formed by $ZrCl_4$ with ethyl, propyl, isobutyl, and benzyl acetates are given in Tables 3-6.

For the complex compound $ZrCl_4 \cdot 2CH_3COOC_2H_5$ the polarization at infinite dilution is 1036 cc, the deformation polarization is 94.41 cc, and the dipole moment is 6.75 D.

The remaining three esterates of zirconium tetrachloride have the following values of the given quantities:

	P_∞	P_D	μ
$ZrCl_4 \cdot 2CH_3COOC_3H_7$	1040 cc	105.18 cc	6.73 D
$ZrCl_4 \cdot 2CH_3COOC_4H_9$	1052 cc	115.82 cc	6.74 D
$ZrCl_4 \cdot 2CH_3COOCH_2C_6H_5$	1062 cc	182.65 cc	6.54 D

TABLE 3

Complex $ZrCl_4 \cdot 2CH_3COOC_2H_5$ in Benzene

P_∞ = 1036 cc, R = 82.11 cc.

C (mole fraction)	ε	d	P_2
0.00318	2.520	0.8846	1083
0.00476	2.651	0.8879	1103
0.00638	2.811	0.8910	1148
0.00962	3.121	0.8973	1148
0.01290	3.476	0.9037	1149
0.01510	3.695	0.9077	1126
0.01970	4.205	0.9165	1091

TABLE 4

Complex $ZrCl_4 \cdot 2CH_3COOC_3H_7$ in Benzene

P_∞ = 1040 cc, R = 91.50 cc

C (mole fraction)	ε	d	P_2
0.00224	2.445	0.8822	1074
0.00337	2.539	0.8845	1116
0.00452	2.629	0.8868	1028
0.00563	2.733	0.8889	1138
0.00863	3.021	0.8949	1161
0.01150	3.310	0.9001	1158
0.01780	3.950	0.9118	1106

TABLE 5

Complex $ZrCl_4 \cdot 2CH_3COOC_4H_9$ in Benzene

P_∞ = 1052 cc, R = 100.58 cc

C (mole fraction)	ε	d	P_2
0.00277	2.491	0.8830	1123
0.00411	2.606	0.8861	1152
0.00595	2.866	0.8915	1181
0.00942	3.105	0.8960	1183
0.01180	3.350	0.9003	1180
0.01710	3.900	0.9099	1140
0.02020	4.149	0.9155	1083

TABLE 6

Complex $ZrCl_4 \cdot 2CH_3COOCH_2C_6H_5$ in Benzene

P_∞ = 1060 cc, R = 158.42 cc

C (mole fraction)	ε	d	P_2
0.00224	2.456	0.8842	1146
0.00347	2.567	0.8874	1201
0.00489	2.699	0.8905	1230
0.00608	2.810	0.8935	1232
0.00910	3.112	0.9006	1235
0.01230	3.446	0.9084	1218
0.01880	4.126	0.9242	1150

The data of Table 7 characterize the dependence of the dielectric constant, density, and polarization on the concentration of the complex $ZrCl_4 \cdot 2C_3H_7COOC_2H_5$ in benzene. Its polarization at infinite dilution is 700 cc, its deformation polarization is 136.45 cc, and its dipole moment is 5.23 D.

For the purpose of calculating the effect of the size of the hydrocarbon radical in the ester on the dipole moment and stability of the complex in solution, the moments (μ) of all zirconium tetrachloride esterates studied by us are listed in Table 8. The dipole moment (μ_1) of the organic component of each complex is also given in Table 8. In the last column the increase in dipole moment, due to complex formation, is shown in the form of the difference between the moment of the complex and that of the polar addend (the ester). Here we assume that the two molecules of addend (A) in a complex of composition $ZrCl_4 \cdot 2A$ lie at an angle of 90° with respect to one another, and that the moment of zirconium tetrachloride is zero. Unfortunately, $ZrCl_4$ is insoluble in nonpolar solvents, and therefore it is as yet impossible to estimate its polarity. However, the tetrahedral structure of the $ZrCl_4$ molecule provides a basis for considering it nonpolar [13].

The data in Table 8 plainly show that the reaction of zirconium tetrachloride with esters of monobasic acids, as in the case of tin and titanium tetrachlorides, leads to the formation of highly polar, complex molecules. The cause of the great increase in the dipole moments of zirconium tetrachloride esterates with respect to the

moments of the corresponding polar addends is the formation of a strongly polarized dative bond between the zirconium and one of the oxygen atoms of the ester. At present it is difficult to say which of the oxygen atoms in the ester – the carbonyl or the alkoxy – is the electron donor. Some experimental data favor the latter [14-17]. However, this point requires further investigation and may be cleared up by study of the optical properties, in particular, the absorption spectra of complex compounds of the type [$MeCl_4 \cdot 2A$].

TABLE 7

Complex $ZrCl_4 \cdot 2C_3H_7COOC_2H_5$ in Benzene.
P_∞ = 700 cc, R = 118.10 cc.

C (mole fraction)	ε	d	P_2
0.00224	2.393	0.8824	762
0.00346	2.466	0.8848	819
0.00535	2.591	0.8884	875
0.00790	2.707	0.8913	915
0.00848	2.838	0.8945	950
0.0121	3.149	0.9011	987
0.0183	3.815	0.9125	1036

Analysis of the data in Table 8 reveals that complex compounds formed by zirconium tetrachloride and esters containing identical acid residues but different alkyl radicals have practically identical incremental dipole moments. This regularity was observed earlier during the investigation of the dipole moments, heats of mixing, and viscosities of complex compounds of $SnCl_4$ and $TiCl_4$ with esters of monobasic acids [17-19]. In our opinion, this constancy of incremental dipole moment indicates that the investigated complex compounds are equally stable in solution and that the size of the alkyl radical has no noticeable effect on their stability.

It is a different matter when we change the molecular weight of the acid residue in the ester. Comparison of the dipole moments of the complex compounds $ZrCl_4 \cdot 2HCOOC_2H_5$ (7.63 D), $ZrCl_4 \cdot 2CH_3COOC_2H_5$ (6.75 D) and $ZrCl_4 \cdot 2C_3H_7COOC_2H_5$ (5.23 D) or $ZrCl_4 \cdot 2HCOOC_3H_7$ (7.76 D) and $ZrCl_4 \cdot 2CH_3COOC_3H_7$ (6.73 D) plainly reveals that as the molecular weight of the acid residue in the ester increases, the moment decreases considerably.

TABLE 8

Complex	μ	μ_1	$\mu - \mu_1\sqrt{2}$
$ZrCl_4 \cdot 2HCOOC_2H_5$	7.63	1.92	4.90
$ZrCl_4 \cdot 2HCOOC_3H_7$	7.76	1.89	5.06
$ZrCl_4 \cdot 2CH_3COOC_2H_5$	6.75	1.81	4.20
$ZrCl_4 \cdot 2CH_3COOC_3H_7$	6.73	1.85	4.10
$ZrCl_4 \cdot 2CH_3COOC_4H_9$	6.74	1.86	4.10
$ZrCl_4 \cdot 2CH_3COOCH_2C_6H_5$	6.54	1.85	3.92
$ZrCl_4 \cdot 2C_3H_7COOC_2H_5$	5.23	1.74	2.76

We observe a similar picture for complex compounds formed by $SnCl_4$ and $TiCl_4$ with esters of monobasic acids [18].

Assuming that complex compounds of the type $ZrCl_4 \cdot 2RCOOR$, are identical in structure and that the moment of the Zr – O dative bond is the same in all cases and does not depend on R or R_1, we can explain the decrease in the dipole moment of the complex with increase in the molecular weight of the acid residue (R) of the ester by an increased degree of dissociation of the complex into its components according to the equation

$$ZrCl_4 \cdot 2RCOOR_1 \rightleftharpoons ZrCl_4 + 2\ RCOOR_1 \text{ or } ZrCl_4 \cdot 2RCOOR_1 \rightleftharpoons ZrCl_4 \cdot RCOOR_1 + RCOOR_1$$

On dilution the equilibrium is displaced to the right, i.e., in the direction of component formation. For confirmation of this, let us consider the dependence of the polarization (P_2) of the following complex compounds on their concentration in benzene:

$$ZrCl_4 \cdot 2HCOOC_2H_5,\ ZrCl_4 \cdot 2CH_3COOC_2H_5 \text{ and } ZrCl_4 \cdot 2C_3H_7COOC_2H_5$$

The polarization of the complex $ZrCl_4 \cdot 2HCOOC_2H_5$ increases on dilution from 1065 to 1246 cc (Table 1). The rapid increase of polarization indicates firstly that the complex $ZrCl_4 \cdot 2HCOOC_2H_5$ is associated, and that the degree of dissociation to monomers of greater polarity than the dimers increases with dilution, and secondly that very little thermal dissociation of the monomeric molecules of the complex occurs within the given con-

centration limits. For the complex compound $ZrCl_4 \cdot 2CH_3COOC_2H_5$ the dependence of polarization on concentration is different in character. Here, at first, the polarization increases on dilution from 1090 to 1149 cc, but on further decrease of concentration it falls to 1083 cc (Table 3). This decrease of polarization at high dilutions is unconditionally explained by the appreciable dissociation of the complex into components, the molecules of which are much less polar than those of the complex itself. This dissociation is most pronounced in the case of the complex formed by $ZrCl_4$ and ethyl butyrate. In this case, as the concentration of the complex decreases, the polarization falls regularly from 1035 to 761 cc (Table 7).

The data given on the dipole moments and polarization of zirconium tetrachloride esterates, which characterize the effect of the molecular weight of the acid residue in the ester on the stability of the complex, are confirmed by the preliminary results of our cryoscopic studies.

Thus, on the basis of literature data and our investigations it may be concluded that the stability of the esterates of zirconium, tin, and titanium tetrachlorides depends not only on the size of the hydrocarbon radical but also on its position in the ester. We are inclined to ascribe the increase in the degree of dissociation of complexes of the type $MeCl_4 \cdot 2RCOOR_1$ with increase in the molecular weight of the acid residue in the ester to the screening effect of the electron donor. The high dipole moments of those complex compounds studied by us, which are formed by zirconium tetrachloride and two molecules of ester, provide a basis for attributing a cis-structure to them. It is true that the calculated dipole moments for cis-forms are somewhat higher than those found experimentally, but we feel that this difference is due to dissociation of the complex into its components.

In conclusion let us note that in the literature known to us we found no data on the dipole moments of coordination compounds of zirconium. In this connection our data may be of some interest.

SUMMARY

1. It has been shown that complex molecules of high polarity are formed in the reaction of zirconium tetrachloride with esters of monobasic acids. The dipole moments of the compounds obtained have been measured (in benzene).

2. The dipole moment of the complex is practically unaffected by variation of the alkyl radical in the ester, but is sharply decreased by increase in the molecular weight of the acid residue. It is concluded from this that the stability of a complex of the type $ZrCl_4 \cdot 2RCOOR_1$ in solution mainly depends on the size of the acid residue.

3. According to the data of dipole-moment measurements complex compounds of zirconium tetrachloride with two molecules of ester have a cis-structure.

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STUDY OF THE COMPOSITION OF C_6 HYDROCARBONS – BY-PRODUCTS OF THE CATALYTIC SYNTHESIS OF DIVINYL FROM ALCOHOL

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The conversion of ethyl alcohol into divinyl over the S. V. Lebedev catalyst [1] is a complex catalytic process accompanied by a considerable number of side reactions. Study of the by-products was begun during the lifetime of S. V. Lebedev [2] and was continued afterwards by a number of investigators [3]. The research of Yu. A. Gorin in the field of catalytic formation of conjugated dienes from alcohols, binary mixtures of the latter, and mixtures of alcohols with aldehydes and ketones [4] made it possible to explain the formation of those by-products which are now known. However, the composition of the by-products has not been fully studied as yet. This refers mainly to those substances which are obtained in such small quantities that their isolation and identification are rendered difficult. Further study of the composition of by-products of the contact synthesis of divinyl from alcohol is important both for a more profound understanding of the mechanism of this industrially important process and for more efficient separation and utilization of these products.

Included among the inadequately-studied by-products are the components of the so-called hexylene–hexadiene fraction obtained in the rectification of hydrocarbons boiling in the 60-90° range. Recently the presence of hexene-2 [2] and hexadiene-2,4 [5] in this fraction was demonstrated, and indications of benzene [3] were obtained.

The present work is devoted to a more detailed study of the composition of the hydrocarbons comprising this fraction.

By rectification of a technical hexylene–hexadiene fraction in laboratory columns having an effectiveness of about 50 theoretical plates, narrow fractions were separated, and these in turn were divided by further distillation into still narrower fractions. In these fractions, besides the substances demonstrated earlier, the following compounds were isolated:

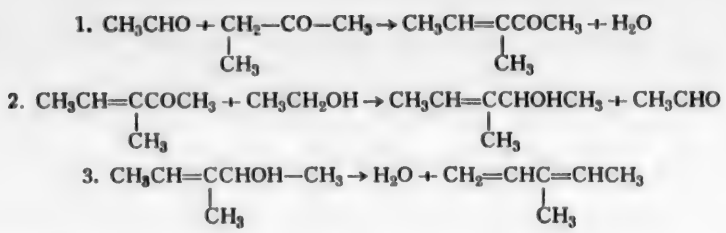
1) Hexadiene-1,3, the physicochemical constants of which agreed with literature data. Its structure was proved by oxidation with potassium permanganate, which gave formic, oxalic, and propionic acids;

2) 3-Methylpentadiene-1,3, which was proved by hydrogenation to 3-methylpentane and oxidation to formic, acetic, and oxalic acids by means of potassium permanganate, and also by formation of an adduct with naphthoquinone, conversion of the adduct to 1,2-dimethylanthraquinone, and oxidation of the latter to 1,2-anthraquinonedicarboxylic acid;

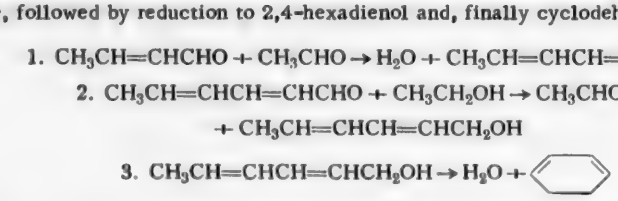
3) Cyclohexadiene-1,3, which was proved by hydrogenation to cyclohexane and oxidation to oxalic and succinic acids by means of potassium permanganate, and also by formation of maleic acid adduct having a characteristic melting point.

The formation of hexadiene-1,3 has already been explained, in an earlier report [6], as the result of the condensation and further transformations of acetic and butyric aldehydes, aided by the S. V. Lebedev catalyst, in the presence of ethyl alcohol.

3-Methylpentadiene-1,3 may be formed in the S. V. Lebedev process by the reaction of acetaldehyde and ethyl methyl ketone.



The formation of cyclohexadiene-1,3 may be the result of the condensation of crotonic and acetic aldehydes to form sorbaldehyde, followed by reduction to 2,4-hexadienol and, finally cyclodehydration of the latter.



According to rough calculations the yield of hexadiene-1,3 amounts to 0.08 wt. % of the decomposed ethyl alcohol, that of 3-methylpentadiene-1,3 is 0.2 wt. %, and that of cyclohexadiene-1,3 is 0.13 wt. %.

EXPERIMENTAL

A technical hexylene-hexadiene fraction boiling in the interval 60-90°, d_4^{20} 0.730, was freed from peroxides by heating with iron filings and a little acid and dried with calcium chloride. After this preliminary treatment the dried product was subjected to fractional distillation in laboratory columns having an effectiveness of about 50 theoretical plates at a reflux ratio of 45-50. The total volume of hexylene-hexadiene fraction distilled was 4860 ml. After a large number of distillations, fractions boiling in a 1-2° range were isolated. For these the density (d_4^{20}), refractive index (n_D^{20}), content of diene hydrocarbons with conjugated bonds (condensation with maleic anhydride), and bromine number (g of Br/ 100 g of fraction) were determined.

Fractions boiling at 73-74, 78-79, and 79-80°, which were obtained in the greatest amounts, were redistilled under the same conditions and studied in greater detail. The results of investigation of the remaining fractions, which contain the substances found earlier, are not given here.

From the 73-74° fraction the 73.1-73.4° fraction was separated: d_4^{20} 0.7097, n_D^{20} 1.4404. Bromine number: 358 (found). C_6H_{10}. 362 (calculated). According to literature data for hexadiene-1,3: b.p. 72.9°, d_4^{20} 0.7070, n_D^{20} 1.4402 [7].

Oxidation of the 73.1-73.4° fraction by potassium permanganate in an alkaline medium gave: formic acid [proved by reduction of mercuric chloride solution and formation of a considerable precipitate of calomel and by the lead salt. Found %: Pb 79.5, 79.7. $(HCOO)_2Pb$. Calculated %: Pb 79.5], oxalic acid [proved by formation and analysis of the calcium salt. Found %: Ca 31.04, 31.03 $(COO)_2Ca$. Calculated %: Ca 31.21] and propionic acid [proved by the silver salt. Found %: Ag 49.86, 59.90. CH_3CH_2COOAg. Calculated, %: Ag 59.67].

From the 78-79° and 79-80° fractions, fractions boiling in the 77.6-78.6, 78.6-79.3 and 79.3-80.1° ranges were separated by successive distillations.

Investigation of the 77.6-78.6° fraction: d_4^{20} 0.7704, n_D^{20} 1.4598. Bromine number: 360 (found). Content of diene hydrocarbons: 95.0%.

According to literature data for 3-methylpentadiene-1,3: b.p. 76-79°, d_4^{20} 0.7452, n_D^{20} 1.4528 [8]; for cyclohexadiene-1,3: b.p. 80.3°, d_4^{20} 0.8413, n_D^{20} 1.4740 [9].

Hydrogenation of the fraction (25.26 g) was done by the S. V. Lebedev method over platinum black in alcoholic solution [10]. The volume of hydrogen used was 13,397 ml. Hydrogen number 478. The calculated hydrogen number of 3-methylpentadiene-1,3 is 491. That of cyclohexadiene-1,3 is 504.

After recovery of the hydrogenated product from the alcoholic solution, drying, and distillation over metallic

sodium the saturated hydrocarbon was fractionated by means of a column with an effectiveness of 30 theoretical plates. Changed to still: 13.8 g. Relative amounts of fractions obtained: 63.0-64.0°, 60%; 65-78.5°, 6.7%; 79.0-80.0°, 11.1%; residue, 14.4%; Losses, 7.7%.

Fraction of hydrogenated product, boiling at 63.0-64.0°: d_4^{20} 0.6652, n_D^{20} 1.3765, MR_D 29.7; calc. 29.9.

Found %: C 83.62, 83.68; H 16.40, 16.30. C_6H_{14}. Calculated %: C 83.72; H 16.28.

The product obtained was identified as 3-methylpentane. Literature data for the latter: b.p. 63.2°, d_4^{20} 0.66409, n_D^{20} 1.3765 [11].

Fraction of hydrogenated product, boiling at 79.0-80.0°: d_4^{20} 0.7740, n_D^{20} 1.4222.

Found %: C 85.68; H 14.51. C_6H_{12}. Calculated %: C 85.72; H 14.28.

Residue: d_4^{20} 0.7790, n_D^{20} 1.4250.

Literature data for cyclohexane: b.p. 80.80°, d_4^{20} 0.77867, n_D^{20} 1.42623 [12].

Formation of adduct with maleic anhydride. On condensation of 3.15 g of the 77.6-78.6° fraction with 4 g of of maleic anhydride in benzene solution, the mixture turned green. The mixture was heated to 70° and the benzene distilled off, after which the residue was washed with hot water. The crystals obtained were repeatedly recrystallized from ether to a constant m.p. of 144°. According to literature data the melting point of the adduct of maleic anhydride with cyclohexadiene-1,3 is 147° [13].

Infrared Absorption Spectra of Hydrocarbons

Obtained absorption maxima (cm^{-1})	Literature data for absorption maxima (cm^{-1})	
	3-methylpentadiene-1,3 [18]	cyclohexadiene-1,3 [19
755		765
843	846	845
905		903
944	945	
990		990
1063		1078
1140	1143	
1167	1169	1164
1230	1235	1234

Condensation of the 77.6-78.6° fraction with α-naphthoquinone and formation of dimethylanthraquinone and anthraquinonedicarboxylic acid.

To 1.51 g of α-naphthoquinone (m.p. 122-123°, recrystallized from petroleum ether) was added 0.9 g of the hydrocarbon, dissolved in 20 ml of ethyl alcohol. The condensation was carried out under the conditions described by B. A. Arbuzov and V. S. Abramov [14]. The reaction mixture was refluxed 4 hours on a water bath. Since the addition product was a tetrahydroanthraquinone derivative, 10 ml of alcoholic potash was added to it, and air was drawn through the reaction mixture in order to convert it to an anthraquinone derivative by dehydrogenation. The resulting product, which amounted to 1.53 g, was repeatedly recrystallized from alcohol and finally obtained in the form of red crystals with an m.p. of 151-153°. Literature data for 1,2-dimethylanthraquinone: m.p. 150° [15].

The dehydrogenation product was oxidized, in accordance with Elbs [16], by heating with nitric acid in sealed tubes at 170° for 2 hours followed by release of gases and then by further heating for 3 hours at 200-220°. Pale, yellow crystals melting at 270° were obtained by recrystallization from glacial acetic acid. According to the literature [17] 1,2-anthraquinonedicarboxylic acid has m.p. 270°.

Found %: C 64.31; H 3.11. $C_{14}H_6O_4(COOH)_2$. Calculated %: C 64.86; H 2.70.

Infrared Absorption Spectrum of the 77.6-78.6° Fraction.*

* We hereby extend our thanks to S. N. Andreev for assistance rendered in this part of the work.

The spectrum was obtained with an IKS-6 infrared spectrometer (1953) having a NaCl prism and provision for automatic recording of the absorption curve in the 730-1300 cm^{-1} range; the sample was held in a KCl cuvette giving a layer thickness of 0.15 mm. In the table below, the recorded absorption maxima are compared with those given in the literature for 3-methylpentadiene-1,3 and cyclohexadiene-1,3. The absorption maxima for 3-methylpentadiene-1,3 were obtained by interpretation of its absorption curve [18].

Investigation of the 78.6-79.3° fraction; d_4^{20} 0.7665, n_D^{20} 1.4601.

On oxidation of the 78.6-79.3° fraction in alkaline solution oxalic acid (proved by formation of the calcium salt) was obtained. When the volatile acids were distilled off, the presence of formic and acetic acids was established (by reduction of mercuric chloride to calomel and formation of ethyl acetate, respectively). After removal of the formic and acetic acids the remaining liquid was evaporated to dryness, and the residue was extracted with ether. After eleimination of the ether and recrystallization from alcohol and then from water an acid with a m.p. of 183° was obtained; a mixture of the latter with succinic acid gave no melting-point depression. Thus formic, acetic, oxalic, and succinic acids were found among the oxidation products.

In the reaction of maleic anhydride with the fraction, crystals with a m.p. of 147°, corresponding to the adduct with cyclohexadiene-1,3, were obtained.

Investigation of the 79.3-80.1° fraction. On oxidation of this fraction by potassium permanganate the same acids were obtained as in the oxidation of the 78.6-79.3° fraction. The reaction of the 79.3-80.1 fraction with maleic anhydride also gave an adduct with a m.p. of 147°.

On the basis of this investigation the 77.6-78.6, 78.6-79.3, and 79.3-80.1° fractions may be regarded as mixtures of 3-methylpnetadiene-1,3 and cyclohexadiene-1,3.

SUMMARY

1. In the hexylene-hexadiene fraction of the by-product hydrocarbons obtained in the catalytic synthesis of divinyl from alcohol by the S. V. Lebedev method, the presence of the conjugated dienes, hexadiene-1,3, 3--methylpentadiene-1,3 and cyclohexadiene-1,3 has been demonstrated.

2. Reaction schemes are suggested to explain the formation of 3-methylpentadiene-1,3 and cyclohexadiene--1,3 under the conditions of the S. V. Lebedev process.

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CONDENSATIONS OF 5-HALOFURFURALS WITH METHYL KETONES

I. CONDENSATION WITH ACETONE

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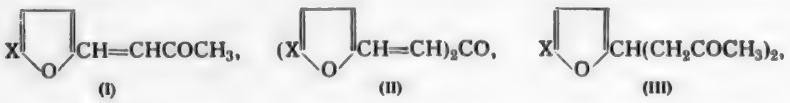
Furfural was first condensed with acetone in an alkaline medium by Schmidt [1]. However, the condensation products, mono- and difurfurylideneacetones, were isolated in pure form by L. Claisen and A. Ponder [2]. V. V. Chelintsev and E. K. Nikitin [3, 4] reported the possibility of the given condensation both in alkaline and acid media. It was established [5] that, in dependence on the relative proportions of components other than the above-mentioned mono- and difurfurylideneacetones, furfurylidenediacetone is also formed. The further condensation of furfural with acetone was studied by a number of authors [6].

Condensations of 5-halofurfurals with acetone and, in general, with methyl ketones are not described in the literature. Having in mind the fact that introduction of halogen atoms into the furfural nucleus in the α-position increases its stability and does not inhibit the reactivity of the aldehyde group [7], and also the fact that the condensation products must be of theoretical as well as practical interest (for instance, in the field of analytical chemistry or as physiologically active preparations), we studied condensations of 5-halofurfurals with acetone both in acid and alkaline media. We found that the reaction takes place only in an alkaline medium. On the basis of the work of V. V. Chelintsev and E. K. Nikitin it was to be expected that when an excess of acetone was used in the presence of alkali, mono(halofurfurylidene)acetones (I) and halofurfurylidenediacetones (III), would predominate, but that with an excess of halofurfurals, di(halofurfurylidene)acetones (II) would predominate.



(I) (II) (III)

where X = Cl, Br, or I.

We carried out the reaction with equimolar quantities, with an excess of halofurfurals, and with an excess of acetone, in an alcoholic or aqueous-alcoholic medium. However, regardless of the ratio of acetone to halofurfural, in the presence of aqueous solutions of caustic alkalis we obtained only di(furfurylidene)acetones (II). In methanol the condensation proceeds smoothly at room temperature without any resinification, with a yield of about 90%. In ethanol the yield is lower. In the absence of solvent, considerable resinification occurs with an excess of acetone.

Sunlight has no substantial effect on the yield of the product, but accelerates the condensation process. The reaction rate decreases on transition from chloro- to bromo- and iodofurfural. The optimum quantity of alkali necessary for condensation increases on transition from chlorofurfural to iodofurfural.

With 2,4-dinitrophenylhydrazine, di(furfurylidene)acetones give the corresponding 2,4-dinitrophenylhydrazones [8] (see table).

Like difurfurylideneacetone, they dissolve in concentrated sulfuric acid with the formation of colors, specific for each di(halofurfurylidene)acetone (see table). On dilution of the acid solutions with water the colors vanish and the original di(5-halofurfurylidene)acetones are precipitated unchanged. These color reactions may be used for the qualitative detection of 5-halofurfurals and the quantitative determination of acetone by the colorimetric

method, in which di(4-halofurfurylidene)acetones advantageously differ from difurfurylideneacetone in their appreciably greater stability, since they do not resinify under the influence of acids or alkalis.

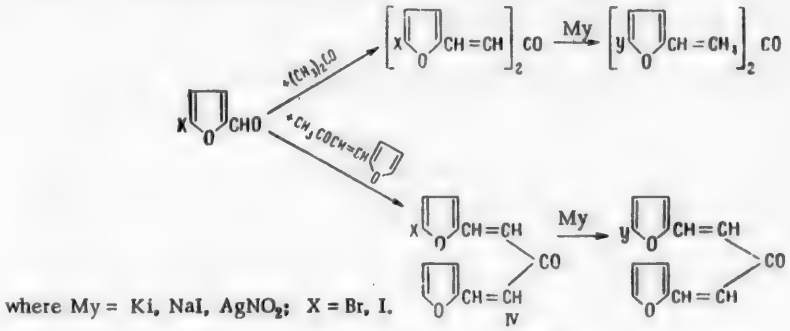
Like all other 5-substitued halogen derivatives of furan, prepared by us [7], di(5-halofurfurylidene)acetones quantitatively evolve halogen on heating with concentrated nitric acid. Di(5-bromofurfurylidene)acetone can take part in an exchange reaction on heating with alkali iodides. The exchange process is easily followed by means of the reaction with H_2SO_4, since the original bromo derivative gives a violet color, and the iodo derivative gives a blue.

The possibility of exchange of halogens for the nitro group has also been shown by us. When the bromo and iodo derivatives were heated with $AgNO_2$ in acetic acid, di(5-nitrofurfurylidene)acetone, identical to the product of condensation of 5-nitrofurfural with acetone [9], was obtained.

We also studied the reaction of 5-halofurfurals with mono- and difurfurylideneacetones. We found that 5--halofurfurals do not displace furfural from difurfurylideneacetone and that, in the case of monofurfurylideneacetone, they condense with the latter to form the corresponding 1-furyl-5-α-halofurylpentadien-1,4-ones-3 (IV); 1-furyl-5-α-bromofurylpentadien-1,4-one-3, when heated with KI in acetic acid, exchanges bromine for iodine.

The most active of the halofurfurals is 5-chlorofurfural, which displaces bromo- and iodofurfurals from the corresponding di(5-halofurfurylidene)ketones (II); bromofurfural displaces iodofurfural. These conversions may easily be followed with the aid of the characteristic colors in sulfuric acid, described above.

The conversions carried out by us are shown in the following scheme.



where My = Ki, NaI, $AgNO_2$; X = Br, I.

EXPERIMENTAL

Condensation of 5-halofurfurals with Acetone*

General procedure: 0.01 mole of the halofurfural (chloro-, brom-, or iodo-) was dissolved in the minimum quantity of methanol (20, 30, or 50 ml, respectively) and 0.012 mole of acetone was added, after which, as the mixture was mechanically shaken in the sun, a 40% aqueous solution of caustic potash (3, 5, or 7 ml of KOH, respectively) was added dropwise at 20-25°.

Within a few minutes after addition of the entire caustic potash solution the condensation product precipitated in the form of glittering crystals. After 10-15 minutes the mixture was transferred to an ice-bath for 0.5 hour and then neutralized with 10% hydrochloric acid (to congo red), after which the precipitate was filtered out, carefully washed with cold water, and dried in a vacuum desiccator over H_2SO_4. The products were purified by recrystallization from methanol (or ethanol), activated charcoal being used. Results are given in the table.

Di(5-halofurfurylidene)acetones are yellow, crystalline substances, easily soluble in hot methanol, ethyl alcohol, and carbon tetrachloride; they are very slightly soluble in petroleum ether and completely insoluble in water.

Exchange Reactions of Di(5-halofurfurylidene)acetones

1. Exchange of bromine and iodine. A mixture of 1.86 g (0.005 mole) of di(5-bromofurfurylidene)acetone, 2 g (0.012 mole) of anhydrous KI, and 10 ml of glacial acetic acid was boiled 0.5 hour in the sun and then poured into 40 ml of water. After 1 hour the precipitate was filtered out and washed with water. B.p. 146-147° (from methanol). A test mixture of the product with di(5-iodofurfurylidene)acetone gave no melting-point depression. The product gave a blue color with HNO_3, iodine was evolved. The 2,4-dinitrophenylhydrazone consisted of glitter-

* With the assistance of L. P. Pozdnysheva.

Characteristics of Difurfurylideneacetones

Difurfurylideneacetones	Empirical formula	Yield (%)	Melting point	Halogen content (in %)		Molecular weight		2,4-Dinitrophenylhydrazones	Nature of color with 80% H_2SO_4	Minimum H_2SO_4 concentration (in %)
				found	calculated	found*	calculated	Melting point		
$(ClC_4H_2OCH{=}CH)_2CO$	$C_{13}H_8O_3Cl_2$	90.8	124—125°	25.43	25.05	270.3	283.12	185—186° (dec.)	Crimson-red	53
$(BrC_4H_2OCH{=}CH)_2CO$	$C_{13}H_8O_3Br_2$	91.4	136—137	42.70	42.96	397.0	372.04	188—189** (dec.)	Violet	56
$(IC_4H_2OCH{=}CH)_2CO$	$C_{13}H_8O_3I_2$	90.5	146—147	54.12	54.46	478.7	466.03	247 (dec.)	Blue	62
$(O_2NC_4H_2OCH{=}CH)_2CO$	$C_{13}H_8O_7N_2$	—	198—200 [9]	—	—	—	—	237—238 (dec.)	Brown	62
$ClC_4H_2OCH{=}CH$ $C_4H_3OCH{=}CH$ >CO	$C_{13}H_9O_3Cl$	90.7	75—76	13.93	14.25	—	248.67	153—155 (dec.)	Red-crimson	50
$BrC_4H_2OCH{=}CH$ $C_4H_3OCH{=}CH$ >CO	$C_{13}H_9O_3Br$	87.7	93—94	27.01	27.26	—	293.13	176 (dec.)	Crimson	50
$IC_4H_2OCH{=}CH$ $C_4H_3OCH{=}CH$ >CO	$C_{13}H_9O_3I$	84.1	129—130	36.82	37.32	348.2	340.13	187 (dec.)	Blue-violet	55

* Molecular weights were determined by two methods – the Beckmann and the Rast.

** Found %: Br 29.32; N 9.86. $C_9H_{12}O_6N_4Br_2$. Calculated %: Br 28.54; N 10.15.

ing, brown-red crystals with a m.p. of 247° (dec. from benzene); a test mixture with di(5-iodofurfurylidene)acetone 2,4-dinitrophenylhydrazone gave no depression (247°).

2. Exchange of halogens for the nitro group. Exchange reactions of bromine and iodine for the nitro group were carried out by the same procedure; a mixture of 0.005 mole of di(5-halofurfurylidene)acetone, 0.02 mole of $AgNO_2$, and 20 ml of glacial acetic acid was allowed to stand for a day and then boiled 1 hour. In both cases di(5-nitrofurfurylidene)acetone with a m.p. of 198-200° (from glacial acetic acid) was obtained.

Condensations of 5-halofurfurals with monofurfurylideneacetone were carried out in a manner analogous to those of 5-halofurfurals with acetone. The condensation products — 1-furyl-5-α-halofurylpentadien-1,4-ones-3 — are yellow, crystalline substances, readily crystallized from methanol, ethyl alcohol, or carbon tetrachloride. Analytical results and the nature of the colors in H_2SO_4 are given in the table.

1-Furyl-5-α-iodofurylpentadien-1,4-one-3 was obtained in two ways: a) by condensation of monofurfurylideneacetone with iodofurfural and b) by the exchange reaction of 1-furyl-5-α-bromofurylpentadien-1,4-one-3 with with KI.

SUMMARY

1. It has been shown that the condensation of 5-halofurfurals with acetone occurs only in an alkaline medium, regardless of the relative proportions of the original components, with the formation of di(5-halofurfurylidene)acetones in yields greater than 90%.

2. Six di-α,β-unsaturated ketones of the furan series, not described in the literature, and their 2,4-dinitrophenylhydrazones have been obtained by the condensation of 5-halofurfurals with acetone and furfurylideneacetone.

3. The minimum sulfuric acid concentrations at which colors, specific for each di(5-halofurfurylidene)acetone and each 1-furyl-5-α-halofurylpentadien-1,4-one-3, are formed, have been found.

4. The possibility of exchange of bromine in di(5-bromofurfurylidene)acetone and 1-furyl-5-α-bromofurylpentadien-1,4-one-3 for iodine and that of exchange of bromine or iodine in di(5-halofurfurylidene)acetones for the nitro group have been shown.

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CONDENSATION OF DIENIC COMPOUNDS WITH METHYL METHACRYLATE

THE SYNTHESIS OF HYDROAROMATIC ALCOHOLS AND HYDROCARBONS

N. P. Sopov and M. L. Kovner

In earlier studies with participation of one of the authors of the present paper, an investigation was made of the possibility of preparing tertiary hydroaromatic alcohols and hydrocarbons from products of condensation of 1,3-dienic hydrocarbons with methyl methacrylate by the action of organomagnesium compounds [1, 2]. It was shown in these studies that the action of methyl magnesium iodide on methyl esters of alkylcyclohexenyl carboxylic acids gives mixtures with a wide boiling range.

Our objective in the present work was to elucidate the composition of the mixtures formed. For the purpose of comparison, we also investigated some products prepared from methyl acrylate.

Our experiments showed that reaction of esters of 1-methylcyclohexene-3-carboxylic acid and its homologs with RMgI gives mixtures of alcohols and ketones, the reaction velocity and the relative yields of alcohols and ketones depending upon the position and number of methyl groups in the ring.

Results of experiments carried out under identical conditions are set forth in Table 1.

The content of original ester in the mixture of products was determined by the Zeisel method, that of alcohol by the Terentyev method. Crystalline products could not be prepared from the ketones by reaction with semicarbazide, 4-nitro- and 2,4-dinitriphenylhydrazines and hydroxylamine. In two cases the conjectured ketones could be isolated by fractional distillation; in all other cases the content of ketones in the mixture was only established by difference. We see from Table 1 that the introduction of a methyl group in the para-position to the ester group does not influence the yield of alcohol. A methyl group in the ortho-position lowers the yield of alcohol.

A methyl group attached to the same carbon atom as the ester group has a particularly marked effect on the yield of alcohol. Introduction of a second methyl group in the ortho-position lowers the yield of alcohol by a factor of approximately 2. These effects are presumably associated with steric hindrance [3].

EXPERIMENTAL

Condensation of dienes with methyl methacrylate. The methyl methacrylate used in the work had b.p. 100-101°, d_4^{20} 0.9444, n_D^{20} 1.4150 [4].

Condensation was carried out in sealed glass tubes in toluene solution in presence of hydroquinone while heating for 15-18 hours at 150-160°. Nearly all of the esters of hydroaromatic acids used in the investigation are described in the literature [2, 5]. The constants of the esters that we prepared were substantially identical with those reported in the literature.

We prepared the methyl ester of 1-methyl-2,5-endoethylenecyclohexene-3-carboxylic acid for the first time. The compounds has a camphorlike odor.

B.p. 104.5-105.5° (20 mm), d_4^{20} 1.0389, n_D^{20} 1.4850, MR_D 49.73; calc. 49.78.

Found %: C 73.54; H 9.19; CH_3O 16.96. $C_{10}H_{13}O(OCH_3)$. Calculated %: C 73.30; H 8.94; CH_3O 17.22.

Preparation of ketones and tertiary alcohols. A solution of 0.1 mole of the appropriate ester in 100 ml of absolute alcohol was added to a solution of organomagnesium compound, prepared from 0.25 atom of magnesium

TABLE 1

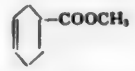
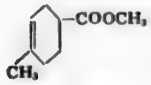
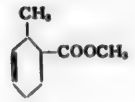
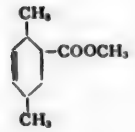
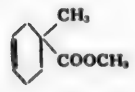
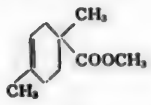
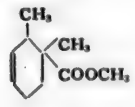
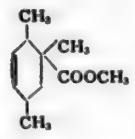
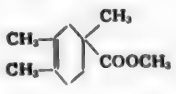
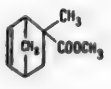
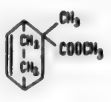
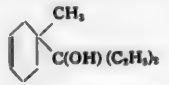
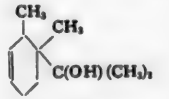
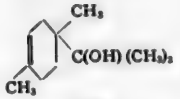
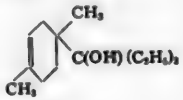
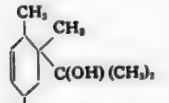
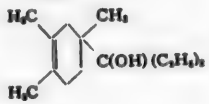
Starting ester	% content in products of interaction of esters with C_2H_5MgI		
	alcohol	ketone	original ester
	100	—	—
	100	—	—
	86	—	14
	57	29	14
	71	22	7
	64	8	28
	29	15	56
	35	7	58
	76	3	21
	54	—	46
	25	42	33

TABLE 2

Alcohols

Compound	Boiling point (20 mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	Found (%) C	Found (%) H	Found (%) OH	Calculated (%) C	Calculated (%) H	Calculated (%) OH
	131.5—132.5°	0.9486	1.4950	56.04	56.47	78.96	11.91	9.64	79.06	12.17	9.32
	111.5—112.5	0.9545	1.4939	51.27	51.85	78.46	12.07	10.36	78.51	11.98	10.10
	117—118	0.9476	1.4915	51.47	51.85	78.73	11.88	9.78	78.51	11.98	10.10
	139—140	0.9407	1.4935	60.70	61.09	79.29	12.53	8.64	79.53	12.32	8.86
	121—122	0.9457	1.4915	55.88	56.47	78.72	12.20	9.26	79.05	12.16	9.32
	149—150	0.9418	1.4955	65.14	65.67	80.17	12.49	7.83	79.94	12.46	8.08

and 0.28 mole of methyl iodide (or ethyl iodide) in 150 ml of absolute ether, with mechanical stirring and heating on a water bath. After completion of the addition of ester, the heating was continued for another 4-5 hours. The mixture was left overnight and then worked up in the usual manner. The ethereal solution was dried with anhydrous sodium sulfate and distilled in vacuo.

The hydroaromatic alcohols are colorless, viscous liquids with a pleasant odor. The ketones are readily mobile, colorless liquids with a characteristic odor.

Constants and analytical data for the newly prepared alcohols are given in Table 2; those for the ketones, in Table 3.

Preparation of hydrocarbons. Dehydration of the tertiary alcohols was effected by heating the alcohol with a $1\frac{1}{2}$ - fold excess of acetic anhydride in sealed glass tubes for 4 hours at 200°. Yield of hydrocarbons 65-70%.

Constants and analytical data for the newly prepared hydrocarbon are given in Table 4.

With the objective of confirming the proposed structure, we tried to dehydrogenate 1,4-dimethyl--1-isopropenylcyclohexene-3 over platinized carbon (Zelinsky's method). Two passes gave the original hydrocarbon (b.p. 79-80° at 20 mm, d_4^{20} 0.8515, n_D^{20} 1.4795).

TABLE 3

Ketones

Compound	Boiling point (20 mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	Found (%) C	Found (%) H	Calculated (%) C	Calculated (%) H
	101—105°	0.9354	1.4765	50.18	50.34	79.47, 79.72	11.02, 11.07	79.46	10.91
	113—114	0.9322	1.4745	50.17	50.34	79.36, 79.32	10.97, 10.86	79.46	10.91

SUMMARY

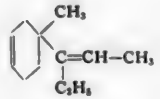
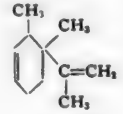
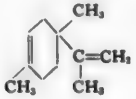
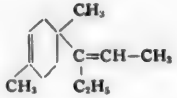
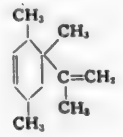
1. The action of methyl magnesium iodide and ethyl magnesium iodide on the products of condensation of methyl methacrylate wtih butadiene, piperylene, isoprene, dipropenyl, diisopropenyl, cyclopentadiene-1,3 and cyclohexadiene-1,3 gave a series of tertiary alcohols and ketones.

2. Dehydration of five alcohols gave the corresponding hydroaromatic hydrocarbons.

3. It was shown in an experiment with 1,4-dimethyl-1-isopropenylcyclohexene-3 that hydrocarbons of this type are not dehydrogenated over platinum, in harmony with the proposed structure.

TABLE 4

Hydrocarbons

Substance	Boiling point (20 mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	Found (%) C	Found (%) H	Calculated (%) C	Calculated (%) H
	98—99°	0.8734	1.4870	54.10	54.48	87.49, 87.35	12.48, 12.22	87.72	12.28
	75.5—76.5	0.8546	1.4773	49.71	49.86	87.63, 87.75	12.39, 12.28	87.93	12.07
	79—80	0.8514	1.4783	49.98	49.86	87.68, 87.71	12.31, 12.32	87.93	12.07
	115—5—117	0.8738	1.4862	58.61	59.10	87.60, 87.49	12.37, 12.51	87.57	12.43
	89.5—90.5	0.8756	1.4855	53.82	54.48	87.52, 87.49	12.58, 12.49	87.72	12.28

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INVESTIGATIONS ON CONJUGATED SYSTEMS

LXXX. INFRARED SPECTRA OF SOME ACETYLENIC AND VINYLACETYLENIC ALCOHOLS

A. A. Petrov and G. I. Semenov

In one of the preceding communications it was shown that a certain parallelism exists between the reactivity of the double bond in molecules of vinylacetylenic hydrocarbons and its activity in infrared spectra [1]. It was of interest to compare these data with results for other classes of vinylacetylenic compounds with conjugated multiple bonds. With this objective we studied the infrared spectra of two representatives of the tertiary vinylacetylenic alcohols for which we had previously established the sequence of addition of bromine [2], hydrogen [3, 4] and alkyl hypohalite [5]. Since the literature contains only few data on the acetylenic alcohols, we also plotted the spectra of some of the primary, secondary and tertiary acetylenic alcohols in our possesion.

The infrared spectra of propargyl alcohol and of six of its homologs have already been described by Wotiz and coworkers [6]. There is a very close similarity in form between our curves and those given in the paper cited for two compounds (propargyl alcohol and heptyn-1-ol-3). There is a slight difference in position of the frequencies reported in the earlier paper [2] and that found by us. These differences are probably due to the fact that we used an LiF prism in this region with a higher resolving power than the NaCl prism used by our predecessor.

Out of all of the spectra obtained, the one most amenable to interpretation is the spectrum of propargyl alcohol since very full information has been published on the vibration spectrum of methylacetylene [7].

The same frequency of 3300 cm^{-1} in both substances corresponds to the valence CH vibrations in the acetylenic grouping. The frequencies in the comparison spectra are slightly different in respect of other valence and deformation CH vibrations. This, too, is understandable, since propargyl alcohol contains a methylene group and methylacetylene, a methyl group. The frequency of the nonplanar CH deformations is presumably superposed on the absorption band originating from the OC group.

One and the same relatively weak band of about 2140 cm^{-1} corresponds to the acetylenic bond. A strong band at about 920 cm^{-1} corresponds to the vibrations of the ν_{C-C} chain.

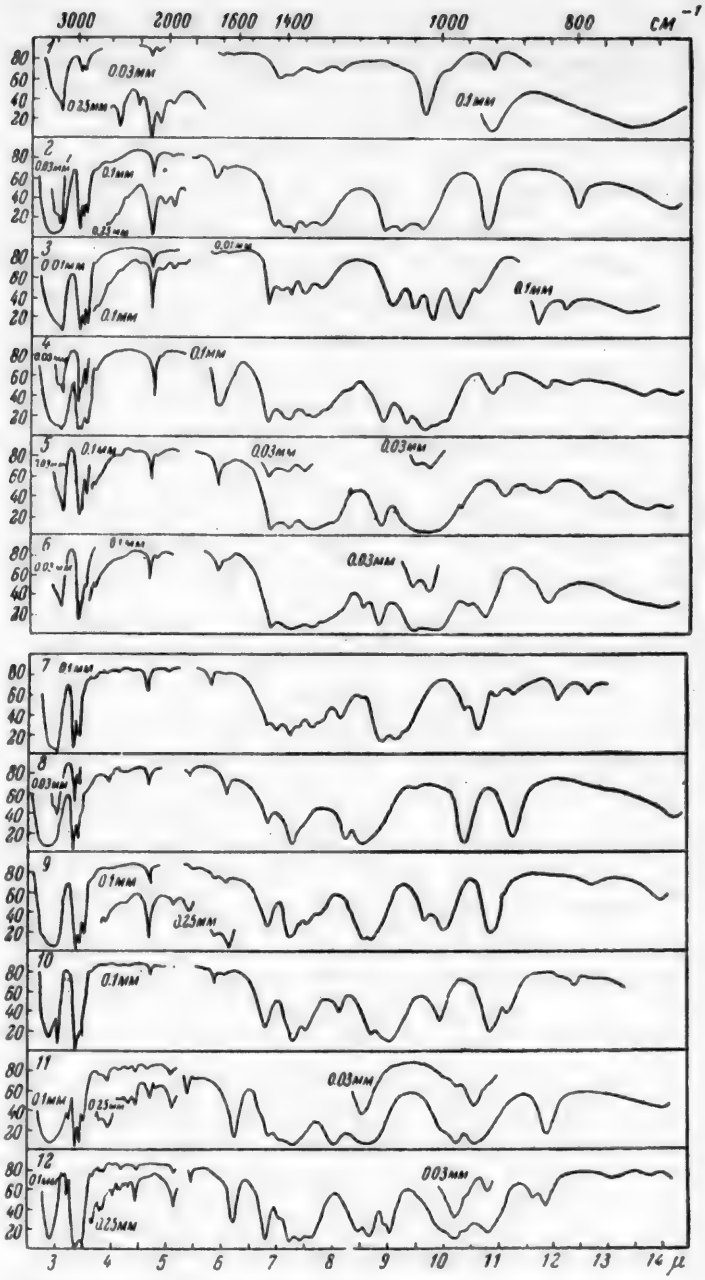
The valence HO vibrations are characterized by a broad band at about 3400 cm^{-1} which is superposed on the band of the valence CH vibrations of the acetylenic grouping; the valence OC vibrations (frequency 1030 cm^{-1}) are extremely intense, presumably due to superposition on the frequency of the nonplanar CH deformations. Saturated primary alcohols have the same frequency of the OC vibrations [7, 8].

Both spectra contain a series of overtones, for example 2070 (2 × 1031), 1299 (2 × 660) cm^{-1}, and proper frequencies, for example 1720, 1232, 1107, 740 cm^{-1}.

Similarity was also found between the spectra of secondary and tertiary alcohols and the corresponding acetylenic hydrocarbons.

Corresponding to the valence vibrations of the triple bond in all cases is a relatively weak band at 2130-2140 cm^{-1}, while corresponding to the C ≡ C — H band is a frequency of about 3300 cm^{-1}.

In the spectra of secondary acetylenic alcohols the valence vibrations of ν_{O-C} are associated with a frequency of about 1070 cm^{-1}. The same frequency is found, however, in the spectra of saturated secondary alcohols. Here there is no longer superposition of this frequency on the frequency of the nonplanar CH deformation, so that its intensity is not exceptional, as in the case of propargyl alcohol.



Infrared transmission spectra.

1) Propargyl alcohol, 2) methylethynyl carbinol, 3) ethylethynyl carbinol, 4) propylethynyl carbinol, 5) butylethynyl carbinol, 6) isobutylethynyl carbinol, 7) methylpropargyl carbinol, 8) dimethylethynyl carbinol, 9) methylethylethynyl carbinol, 10) methyl--tert.-butylethynyl carbinol, 11) dimethylvinylethynyl carbinol, 12) diisopropylvinylethynyl carbinol.

TABLE 1

Infrared Spectra of Propargyl Alcohol and Secondary Acetylenic Alcohols $CH \equiv C - CHOH - R$

	Value of R				
	CH_3	C_2H_5	C_3H_7	C_4H_9	C_4H_9-iso
3390 (vs)	3395 (vs)	3395 (vs)	3395 (vs)	3395 (vs)	3395 (vs)
3300 (vs)	**3289** (vs)	**3289** (vs)	**3289** (vs)	**3289** (vs)	**3289** (vs)
—	2976 (s)	2967 (s)	2967 (s)	2967 (s)	2967 (s)
2950 (s)	2933 (s)	2933 (s)	2933* (s)	2941* (s)	2933* (s)
2725* (w)	2725* (w)	2725* (w)	2732* (w)	2732* (w)	2710* (w)
—	2558 (w)	2558* (w)	2684 (w)	—	—
2445 (w)	2445 (w)	2427* (w)	—	2415 (w)	2381* (vw)
2242 (vw)	2353* (vw)	2227 (vw)	—	—	—
2141 (m)	**2137** (m)	**2128** (m)	**2110** (m)	**2137** (m)	**2132** (m)
2070 (m)	2105 (w)	2053 (m)	—	2075 (w)	2075* (w)
1969 (vw)	1969 (vw)	—	—	—	—
—	1852 (w)	1887* (w)	—	—	—
1721 (m)	1715 (m)	1709 (w)	1689 (m)	1695 (m)	1695 (m)
—	1453 (s)	1464 (s)	1464 (s)	1464 (s)	1464 (s)
1429 (s)	1418 (s)	1412 (s)	—	—	—
1381* (s)	1374 (s)	1385 (s)	1389 (s)	1385 (s)	1385 (s)
—	1326 (s)	1339 (s)	1307 (s)	1335 (s)	1304 (s)
1299* (s)	1289 (s)	1282 (s)	1269* (s)	1244* (s)	1282* (s)
1232 (s)	—	—	1169* (s)	—	—
1107* (m)	1116 (s)	1103 (s)	1118 (s)	1126 (s)	1172 (s)
—	—	—	—	—	1136 (s)
—	**1082** (s)	**1079*** (s)	**1068** (s)	**1053** (s)	**1060** (s)
1031 (vs)	1040 (s)	1053 (s)	1033 (s)	1021 (s)	1025 (s)
—	—	1019 (s)	1014* (s)	—	—
984* (m)	—	973 (s)	991* (s)	969* (s)	960 (s)
917 (s)	922 (s)	932 (m)	916 (m)	900 (m)	929 (s)
—	—	855 (m)	840 (m)	845 (m)	838 (s)
—	802 (m)	814 (m)	810 (m)	—	-
—	—	—	—	784 (m)	—
740 (sd)	—	741 (md)	738 (md)	730 (s)	—
—	704 (m)	—	701 (m)	708* (s)	707 (s)

* Starred frequencies are overtones of other, more differentiated, frequencies.

TABLE 2

Infrared Spectra of Tertiary Acetylenic and Vinylacetylenic Alcohols

$(CH_3)(R)COH—C\equiv CH$			$R_2COH—C\equiv C—CH=CH_2$	
Value of R				
CH_3	C_2H_5	$C(CH_3)_3$	CH_3	$(CH_3)_2CH$
3400 (s)	3400(s)	3472 (s)	3400(s)	3448 (s)
3300 (s)	3300(s)	3289 (s)	—	—
	—	—	3106(s)	3106*(m)
2985 (s)	2985(s)	2985 (s)	2985(s)	2985 (s)
2933 (s)	2933(s)	2933*(s)	2933(s)	2933 (s)
—	—	—	—	—
2874* (m)	2865(s)	2865 (s)	2865(s)	2865 (s)
—	—	—	—	—
2841* (w)	2725 (w)	2725 (w)	2725*(w)	2725*(w)
2577 (w)	2577*(w)	2591 (w)	2646*(w)	2591*(w)
—	2251 (w)	2451 (w)	2506 (w)	2445 (w)
2315 (vw)	2315 (vw)	2315 (w)	2315 (w)	2315 (w)
2132 (w)	2128 (w)	2128 (w)	2232 (w)	2212 (w)
—	—	—	—	—
1953 (vw)	1934 (w)	1969 (w)	1946 (w)	1942 (w)
1884 (w)	1835 (w)	1848 (w)	1835 (m)	1842 (m)
1721 (w)	1704 (w)	1706 (m)	—	—
1639 (m)	1634 (m)	1626 (w)	1603 (s)	1605 (s)
1460 (s)	1460 (s)	1479 (s)	1456 (s)	1468 (s)
—	—	—	1414*	1414*(s)
1372 (s)	1376 (s)	1370 (s)	1368 (s)	1381 (s)
1330* (s?)	1326 (s)	1324 (s)	—	1342 (s)
—	1265 (s)	--	—	1307 (s)
1212 (s)	—	1229 (s)	1241 (s)	—
1171 (vw)	1163 (s)	1151 (s)	1168 (vs)	1176 (s)
—	1139 (s)	—	—	1148 (s)
—	—	1107 (s)	—	1105 (s)
1053 (w)	1035 (s)		—	—
—	1997 (s)	1006*(s)	997* (s)	—
—	—	—	974 (s)	977 (vw)
962 (s)	917 (s)	1988(s)	—	960* (s)
—	—	—	945 (vs)	923 (s)
885 (s)	906*(s)	895(s)	842 (s)	858 (m)
—	—	—	—	840 (m)
—	787 (w)	807 (m)	—	760 (w)
700 (m)	713 (m)	—	711 (m)	726 (w)

Note: There are some additional weak frequencies (4.17, 4.72 and 4.82 μ) in the 4-5μ region in the case of the last two alcohols.

The spectrum of the β-substituted acetylenic alcohol, pentyn-1-ol-4, differs from that of the α-substituted isomer, pentyn-1-ol-3, in not containing a frequency of about 2870 cm^{-1}, in having a higher absorption in the 1100 and 950 cm^{-1} regions, and in having a lower frequency in the 1050 cm^{-1} region [9].

The band of the valence HO vibrations in the case of tertiary alcohols is somewhat more separated from the band of the CH vibrations. This is particularly true of methyl-tert.-butylethynyl carbinol. This differentiation of the frequencies is caused by shifting of the band of the valence HO vibrations toward the short-wave region, probably due to reduced association owing to steric hindrance. The 1170 cm^{-1} frequency corresponds to the ν_{O-C} vibrations in the spectra of tertiary saturated and acetylenic alcohols. In the case of dimethylethynyl carbinol, we again observed an anomalously high intensity of this frequency due to superposition.

A frequency of about 920 cm^{-1} occurs in the spectra of all of the alcohols and is presumably caused by ν_{C-C} vibrations.

All of the acetylenic alcohols have characteristic absorption bands at about 1700 cm^{-1}, as well as some in the 1650 cm^{-1} region which are usually of medium intensity. The first of these two frequencies was detected in the spectra of many acetylenic compounds. The first of these two frequencies was detected in the spectra of many acetylenic compounds. The nature of these frequencies is uncertain. They are possibly constituted from the $\delta_{C\equiv C-C}$ and $\delta_{C\equiv C-H}$ frequencies.

The literature contains data on the Raman spectrum of dimethylethynyl carbinol [10]. The frequencies in both of the spectra are identical or very close. In respect to the position in the spectra of the frequencies of the double and triple bonds, vinylacetylenic alcohols also do not differ from hydrocarbons of corresponding structure [1, 11]. The frequency of 1650-1700 cm^{-1} characteristic of acetylenic compounds is here not detected. It is probably masked by the frequency of the double bond. The vinyl group is characterized by the usual frequencies: 3106 (valence CH vibrations), 1942 and 1845 (overtones), 1603 (valence vibrations of the double bond), 975 and 920-945 cm^{-1} (deformation CH vibrations). A conspicuous feature is the abnormally high value of the latter frequency in the case of dimethylvinylethynyl carbinol. This frequency is presumably shifted due to superposition of the frequency corresponding to the chain vibrations. This explanation is supported by its abnormally high intensity.

The intensity of the frequencies of the double bond in both of the vinylacetylenic alcohols is extremely high, and reflects its high degree of polarity. This is in harmony with the sequence of addition of bromine [2] and hypohalites [5] to vinylacetylenic alcohols: preferential addition occurs at the double bond. Catalytic addition of hydrogen, on the other hand, takes place at the more polarizable triple bond [3, 4].

Data on the dipole moment of dimethylvinylethynyl carbinol have been published [12]. Its magnitude does not differ from that found for saturated alcohols. Consequently, the conjectured shift of the electron cloud toward the double bond is not reflected in the magnitude of the dipole moment.

EXPERIMENTAL

We obtained propargyl alcohol from the "Buna-Werke" (b.p. 112°; n_D^{20} 1.4302). Dimethylvinylethynyl carbinol with b.p. 52° (10 mm) and n_D^{20} 1.4780 was used. Both of the alcohols were purified by rectification. Secondary alkylpropargyl alcohols were prepared from propiolaldehyde by the organomagnesium synthesis [13]. Tertiary acetylenic alcohols were prepared from the corresponding ketones and sodium acetylide in liquid ammonia. Dimethylethynyl carbinol had b.p. 103°, n_D^{20} 1.4195. Methylethylethynyl carbinol had b.p. 70.5-71.5° (10 mm), n_D^{20} 1.4309. Methyl-tert.-butylethynyl carbinol had b.p. 84.5-85.5° (10 mm), n_D^{20} 1.4389. Methylpropargyl carbinol was obtained from propylene oxide and sodium acetylide [9]. Diisopropylvinylethynyl carbinol was prepared by the organomagnesium synthesis from vinylacetylene and isobutyrone [2].

The infrared transmission spectra were plotted with the IKS-2 two-ray spectrograph in the 3-5 μ range with an LiF prism, and later with a NaCl prism. Layer thickness 0.03, 0.1 and 0.25 mm. Evaluation was on the basis of wavelength. The accuracy of reading was 0.01-0.02 μ.

Results of measurements are given in the diagram and in Tables 1 and 2. The most important frequencies are printed in bold type in the tables.

SUMMARY

1. The infrared spectra of 9 acetylenic and 2 vinylacetylenic alcohols were examined.

2. The principal regularities in these spectra were noted on the basis of the usual measurement of frequencies.

3. A relation was found between reactivity of vinylacetylenic alcohols and the intensity of the absorption bands corresponding to the multiple bonds.

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INVESTIGATIONS ON CONJUGATED SYSTEMS

LXXXI. INFRARED SPECTRA OF SOME α,β-UNSATURATED ACETYLENIC ALDEHYDES AND KETONES

A. A. Petrov and G. I. Semenov

Examination of the infrared spectra of vinylacetylenic hydrocarbons has shown that conjugated double bonds bring about shifting of the corresponding absorption bands toward the long-wave region. Observations were made at the same time of certain new regularities in the position and intensity of these and other frequencies due to the action of the attached radicals on the conjugated system [1]. It was of interest to compare these spectra with the spectra of α,β-unsaturated acetylenic aldehydes and ketones which also contain a double and triple bond in the conjugated state, but the double bond is distinguished by its well-marked polarity.

With this objective we examined the infrared spectra of propiolaldehyde, butynol, and four ketones with the general formual $R-C\equiv C-CO-CH_3$. There is a very extensive literature on the infrared spectra of carbonyl compounds [2, 3]. Adequate study has also been made of the spectra of α,β-unsaturated olefinic aldehydes and ketones. A shift of approx. 40 cm^{-1} in the absorption band of the carbonyl group in the latter is observed in comparison with saturated compounds; a shift of the frequency of the double bond by approx. 20 cm^{-1} in comparison with olefins is also observed [2-4].*

Some authors claim to have detected additional absorption at 1210-1325 cm^{-1} in the spectra of carbonyl compounds of the aliphatic series; it is difficult, however, to identify these bands with sufficient accuracy [2].

Bands are attributed to the aldehydic hydrogen in the 2700-2900 cm^{-1} (vibration), 1325-1440 cm^{-1} and 780-900 cm^{-1} (deformation) regions.

In the region of the principal frequency of the carbonyl group (about 1700 cm^{-1}), saturated and olefinic compounds do not exhibit any considerable absorption. Many acetylenic compounds absorb in this region, but not so strongly as to mask the extremely strong frequency of the carbonyl group.

Comparison of the spectra of the substances that we examined (see diagram and Table 1) with the spectra of other aldehydes and ketones, also with the spectra of vinylacetylenic hydrocarbons, enables us to reach the following conclusions.

The infrared spectrum of propiolaldehyde contains, in all, 8 fairly strong frequencies. They can all be unequivocally related to definite vibrations on the basis of frequencies reported in the literature for methylacetylene and acetaldehyde [5]: 3289 (ν_{CH} in the acetylenic grouping), 2890 (ν_{CH} in the aldehyde grouping), 2114 ($\nu_{C\equiv C}$), 1701 ($\nu_{C=O}$), 1393 (δ_{CH}), 956 (ν_{C-C}), 827 (δ_{CH} in the aldehyde group) and 746 (?) cm^{-1}. The last frequency occurs in the spectra of many acetylenic compounds containing the $C\equiv C-H$ grouping. It originates possibly from superposition of the $\delta_{C\equiv C-C}$ or $\delta_{C\equiv C-H}$ frequencies on certain other frequencies.

In addition to the frequencies enumerated above, the spectrum of propiolaldehyde contains 8 weak and medium-strong frequencies which are either overtones ($3500 = 2 \times 1701$; $2740 = 2 \times 1393$; $1890 = 2 \times 956$) or fundamental frequencies (3077, 2653, 2048). Especially noteworthy is the frequency of 2740 cm^{-1} which is extremely characteristic of aldehydes and may serve for analytical purposes [6].

The spectrum of butynol is rather more complicated; the majority of the 12 most intensive frequencies can,

* After the present work had been completed, a short paper [12] became known to the authors.

however, also be correlated with specific vibrations: 3300 (ν_{CH} in the acetylenic grouping), 2994, 2915 (ν_{CH} in the CH_3 group), 2114 ($\nu_{C\equiv C}$), 1695 ($\nu_{C=O}$), 1427, 1364 and, probably 1277 (δ_{CH} in the CH_3 group), 1203 (?), 1025 (δ'_{CH} in the CH_3 group), 978 (ν_{C-C}) and 758 (?) cm^{-1}.

TABLE 1

Infrared Spectra

HC≡C–CHO	Compounds R–C≡C–CO–CH_3 where R is				
	H	CH_3	C_2H_5	C_3H_7	C_4H_9
3289 (s)	**3300** (s)	3322 (m)	3322 (m)	3322 (m)	3322 (m)
9077 (m)	3021 (m)	3021 (m)	—	—	—
—	2994 (s)	2985 (s)	2994 (s)	2985 (s)	2994 (s)
—	2915 (s)	2933 (s)	2941 (s)	2950 (s)	2950 (s)
2890 (s)	—	2857 (m)	2882 (s)	2882 (s)	2882 (s)
2740 (m)	2732* (vw)	2732* (w)	2725 (w)	2740 (w)	2740* (w)
2653 (w)	2625 (vw)	2625 (w)	2604 (w)	2632 (w)	2646 (w)
—	2519 (vw)	2469 (w)	2451 (w)	2451 (w)	2469 (w)
—	2342 (vw)	2299 (w)	2294 (w)	2299* (w)	2304 (w)
—	2237 (vw)	**2242** (s)	**2237** (s)	**2237** (s)	**2242** (s)
2114 (s)	**2114** (s)	2165 (m)	2160* (m)	—	2110* (vw)
2028* (m)	—	2033* (vw)	2049 (w)	2075* (w)	2058 (w)
—	1953 (w)	—	1965 (w)	1955 (w)	1953 (w)
1890 (m)	1873 (w)	1924 (w)	1890 (w)	1923 (w)	1912 (vw)
1701 (s)	**1695** (s)	**1681** (s)	**1689** (s)	**1683** (s)	**1681** (s)
—	—	—	1456* (s)	1456* (s)	1468* (s)
—	1427 (s)	1433 (s)	1433 (s)	1433 (s)	1433 (s)
1393 (s)	1364 (s)	1368 (s)	1368 (s)	1357 (s)	1368 (s)
—	—	—	1318 (s)	1330* (s)	1330* (s)
—	1277 (s)	1280 (s)	1280 (s)	1276* (s)	—
1205 (m)	1203 (s)	1241 (s)	1241 (s)	1248 (s)	1248 (s)
—	—	1168* (m)	1174* (m)	—	—
—	—	—	1142* (m)	—	—
1126* (m)	1119 (w)	1116 (m)	1124* (m)	—	1115 (m)
—	1056* (m)	1079* (m)	1074 (s)	1078 (m)	1064 (m)
1045* (m)	—	—	—	1052* (m)	—
—	1025 (s)	1019 (s)	1021 (s)	1021 (s)	1012 (m)
—	—	—	—	1002* (s)	—
956 (s)	978 (s)	965 (s)	971 (s)	952 (s)	973 (s)
—	—	—	908 (s)	880 (m)	871 (w)
827 (m)	—	826 (w)	—	843 (w)	—
—	—	773 (w)	779 (s)	785 (m)	789 (w)
746 (s)	758 (s)	729 (m)	—	732 (m)	743 (w)
—	—	—	—	686 (m)	730 (w)

Consequently, the acetylenic grouping in the spectrum of butynol corresponds to the same frequencies as in the spectrum of propiolaldehyde. The carbonyl group, however, is characterized by a slightly lower frequency. The latter characteristic is also observed in a series of saturated carbonyl compounds [2].

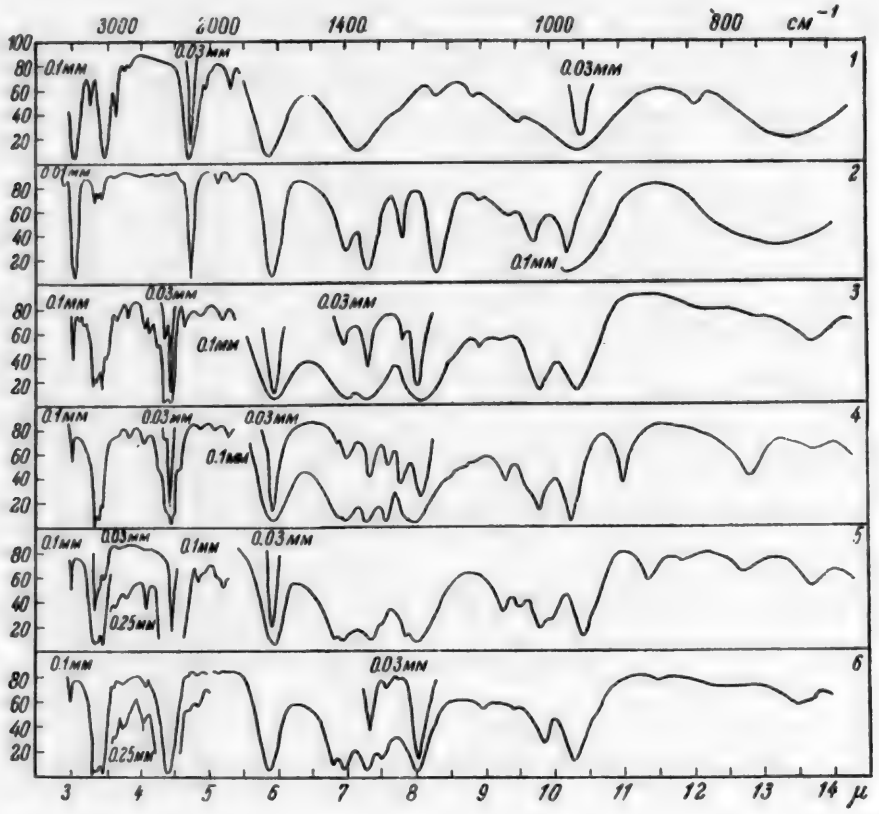
In the spectra of the remaining acetylenic compounds, the same frequency as in the butynol spectrum corresponds to the carbonyl group, and is similar in magnitude to that previously found in the Raman spectrum. Here the frequency of the triple bond has another value (about 2240 cm^{-1}), which is also close to that found in the Raman spectrum. This change of frequency is associated with change in the type of substitution.

In the region of about 3320 cm^{-1}, these ketones have a sharply demarcated band of low intensity. This is most probably an overtone of the $\nu_{C=O}$ frequency. There is no reason for assuming that this frequency is caused by the hydroxyl group resulting from keto–enol rearrangement since typical keto–enols do not absorb in this region [3].

The valence CH vibrations in the radicals are represented in the spectra by the usual frequencies of 2990,

* Starred frequencies are overtones of other, more well-developed, frequencies. The most important frequencies are printed in bold type in the tables.

2950 and 2880 cm^{-1}. To the deformation CH vibrations correspond frequencies of about 1430, 1364 and (apparently) 1280 cm^{-1}. A still higher and a still lower frequency (1460 and about 1330 cm^{-1}) are developed in the spectra of ketones containing a CH_2 group. This was also observed for other series of compounds. The nonplanar CH deformations may be assigned frequencies in the 1010-1025 cm^{-1} region. All of the ketones absorb at about 960-970 cm^{-1} (probably ν_{C-C}). With increasing length of hydrocarbon radical, the number of frequencies in the 700-900 cm^{-1} region increases.



Infrared transmission spectra.
1) Propiolaldehyde, 2) butynol, 3) pentyn-3-one-2, 4) hexyn-3-one-2,
5) heptyn-3-one-2, 6) octyn-3-one-2.

In comparison with acetylenic hydrocarbons of similar structure [2], as well as with alcohols and halogenated derivatives [7, 8], a slight shift and a strong rise in intensity of the $\nu_{C\equiv C}$ bands is observed in the spectra of acetylenic aldehydes and ketones due to conjugation.

The carbonyl group in acetylenic aldehydes and ketones has a frequency 30-40 cm^{-1} lower than in saturated compounds.

Comparison between the $C\equiv C-C=O$ and $C\equiv C-C=C$ systems points to their similarity. The frequencies in the spectra of both classes corresponding to the triple bond are similar in magnitude and slightly lower than those of the saturated compounds (the effect is more pronounced in the spectra of aldehydes and ketones than in the spectra of hydrocarbons) and have a high intensity, especially in the $C\equiv C-C=O$ system. Both systems undergo a considerable lowering of the frequencies corresponding to the double bonds in comparison with saturated compounds. Judging by the rise in intensity of the $\nu_{C\equiv C}$ absorption band, the influence of the carbonyl group on the triple bond is stronger than its influence on the double bond, evidently due to its inherently high polarity and the high polarizability of the triple bond.

EXPERIMENTAL

The methods of preparation of propiolaldehyde, butynol and other ketones have been described in the literature [9-11]. Constants of the compounds with which this investigation was carried out are presented in Table 2.

TABLE 2

Compound	Boiling point	Pressure in mm	d_4^{20}	n_D^{20}
CH≡C—CHO	54 —55°	750	0.9150	1.4070
CH≡C—CO—CH_3	83.5—84.5	750	0.8790	1.4070
CH_3—C≡C—CO—CH_3	56 —56.5	50	0.8957	1.4409
C_2H_5—C≡C—CO—CH_3	68 —68.5	50	0.8778	1.4410
C_3H_7—C≡C—CO—CH_3	83 —83.5	50	0.8719	1.4452
C_4H_9—C≡C—CO—CH_3	101	50	0.8652	1.4478

The infrared spectra were measured with a double-beam IKS-2 spectrograph in the 2.5-3.2 μ range using a prism of LiF, and later using a prism of NaCl. Evaluation was performed on the basis of wavelengths at cell thicknesses of 0.03, 0.1 and 0.25 mm. The accuracy of reading of the divisions of the drum corresponded to 0.01-0.02μ.

Experimental results are shown in Table 1 and in the diagram.

SUMMARY

1. An examination was made of the infrared spectra of propiolaldehyde, butynol, pentyn-3-one-2, hexyn-3-one-2, heptyn-3-one-2 and octyn-3-one-2.

2. It was shown that the conjugated C≡C—C=O system is similar to the C≡C—C=C system. The carbonyl group was found to have a greater influence on the absorption due to the triple bond than on the absorption due to the double bond.

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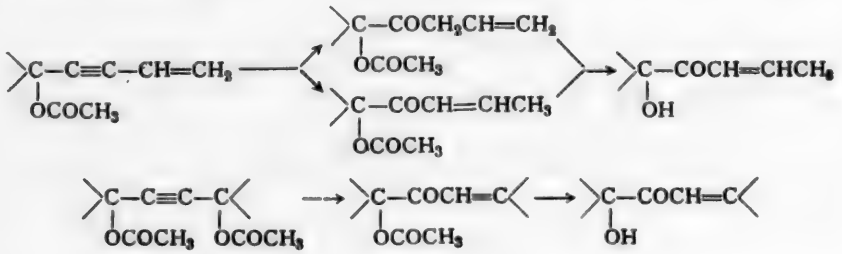
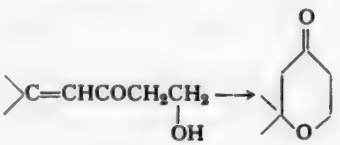
188. CYCLIZATION OF UNSATURATED α-KETOALCOHOLS AND OF 2-KETO-1,4-DIOLS TO TETRAHYDROFURAN-3-ONES

I. N. Nazarov* and S. G. Matsoyan

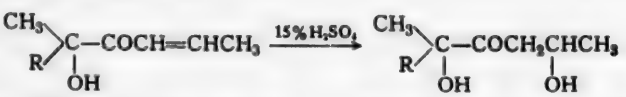
In previous papers we described the preparation of diverse unsaturated α-ketoalcohols by hydration of acetates of vinylethynyl carbinols and diacetates of acetylenic γ-glycols followed by direct or indirect hydrolysis of the unsaturated α-acetoxyketones [1].



As is well known, unsaturated β-ketoalcohols cyclize with facility to tetrahydro-γ-pyrones, even in the instant of formation, under the action of dilute acids [2].



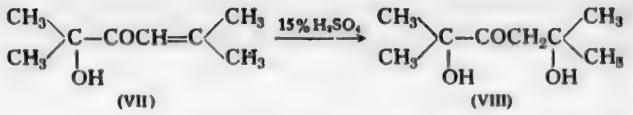
Due to their difficult accessibility, aliphatic unsaturated α-ketoalcohols have not previously been investigated. It was of interest to study the behavior of unsaturated α-ketoalcohols in presence of dilute acids. It was found that, in contrast to the behavior of unsaturated β-ketoalcohols, unsaturated α-ketoalcohols are incapable of cyclization when heated with dilute sulfuric acid; addition of water instead occurs at the double bond with formation of α,β'-ketodiols. For example, heating (50-70°) of unsaturated α-ketoalcohols (I, II and III) with 10-15% sulfuric acid gives the corresponding α,β'-ketodiols (IV, V and VI) in a yield of about 60%.



(I) R = CH_3, (II) R = C_2H_5, (III) R = n-C_3H_7. (IV) R = CH_3, (V) R = C_2H_5, (VI) R = n-C_3H_7

The unsaturated α-ketoalcohol (VII), containing a disubstituted vinyl group, is likewise capable of adding on water under similar conditions, with formation of the α,β'-ketodiol (VIII).

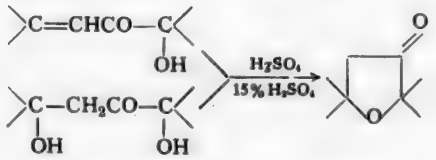
* Deceased.



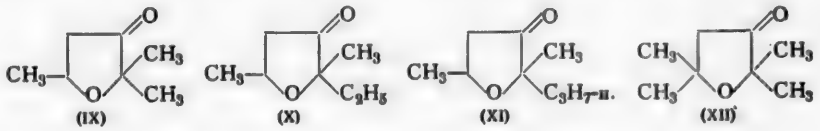
(VII) (VIII)

The prepared α,β'-ketodiols are colorless glycerol-like liquids which distil in vacuum without decomposition. When heated in presence of dehydrating agents, these ketodiols split off water at the expense of the β-hydroxyl group with formation of the original unsaturated α-ketoalcohols. Their diacetates can be obtained by cautious acetylation of the ketodiols with the help of acetic anhydride in presence of traces of sulfuric acid.

The process of hydration of the double bond with the help of 10-15% sulfuric acid is not accompanied by cyclization of the unsaturated α-ketoalcohols to tetrahydrofuran-3-ones even on boiling of the reaction mixture. In presence, however, of a catalytic quantity of mercuric sulfate, the reaction goes in the direction of cyclization and of formation of tetrahydrofuran-3-ones. Cyclization of α,β'-ketodiols to tetrahydrofuran-3-ones goes even more easily under the same conditions.

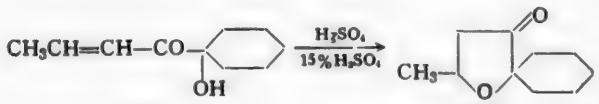


Tetrahydrofuran-3-ones (IX, X, XI and XII) were obtained in high yield by cyclization by this method of the unsaturated α-ketoalcohols (I, II, III and VII) or of the ketodiols (IV, V, VI and VIII).

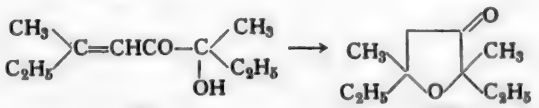


(IX) (X) (XI) (XII)

The unsaturated α-ketoalcohols (XIII and XIV) are likewise easily cyclized to furanones (XV and XVI) on heating (60-80°) of the unsaturated α-ketoalcohols (XIII and XIV) with dilute sulfuric acid in presence of mercuric sulfate.

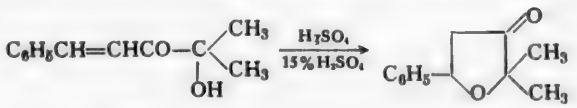


(XIII) (XV)

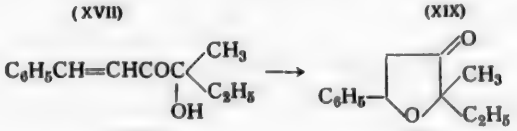


(XIV) (XVI)

Cyclization under the above-described conditions of the unsaturated α-ketoalcohols (XVII and XVIII), prepared by the method of Scheibler and Fischer [3], leads to formation of furans (XIX) and (XX) in good yields.

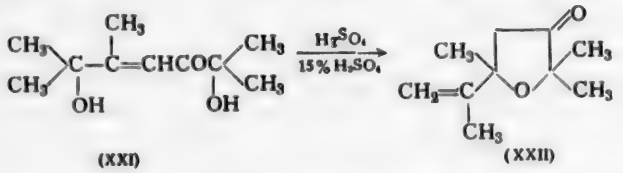


(XVII) (XIX)



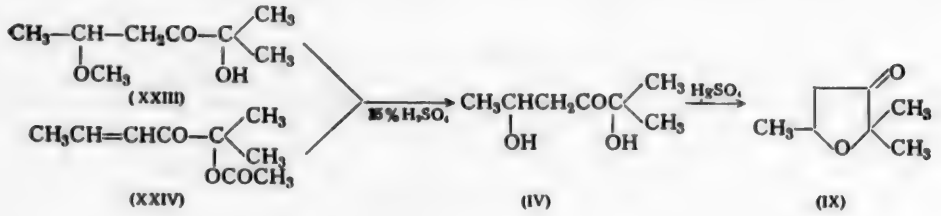
(XVIII) (XX)

Cyclization under similar conditions of the ketoglycol (XXI), obtained by condensation of dimethylacetyl carbinol, is accompaneid by a dehydration reaction which leads to the unsaturated furanone (XXII).



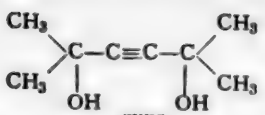
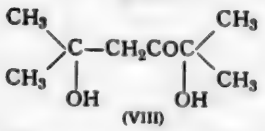
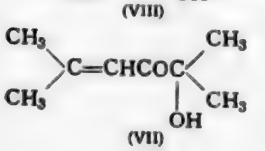
(XXI) (XXII)

Ethers of unsaturated α-ketoalcohols or α,β'-ketodiols likewise undergo cyclization to furanones when treated with dilute sulfuric acid in presence of mercuric sulfate. Thus, for example, hydrolysis of the β-methoxyketol (XXIII) and of the α-acetoxyketone (XXIV) with the help of 15% sulfuric acid in presence of mercuric sulfate leads to formation of the above-described furanone (IX).



(XXIII) (XXIV) (IV) (IX)

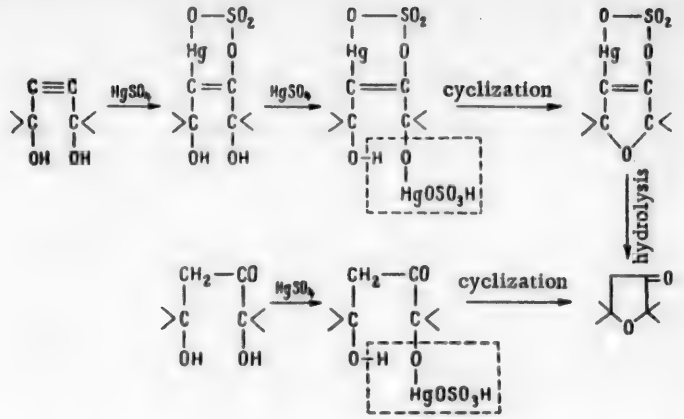
Cyclization of unsaturated α-ketoalcohols or α,β'-ketodiols with the help of mercuric sulfate is accompanied by formation of a yellowish-grey complex which interferes with the working-up of the product and isolation of the tetrahydrofuran-3-ones. In the majority of cases the furanones were therefore isolated from the reaction mass by distillation in steam. Cyclization of α-ketodiols appears to proceed via α,β'-ketodiols; the latter form mercury complexes which are transformed into the corresponding tetrahydrofuran-3-ones.

Starting compound	Yield of furanone (XII)	
	with $HgSO_4$	with $Hg(OCOCH_3)_2$
 (XXV)	98	90
 (VIII)	85	0
 (VII)	80	0

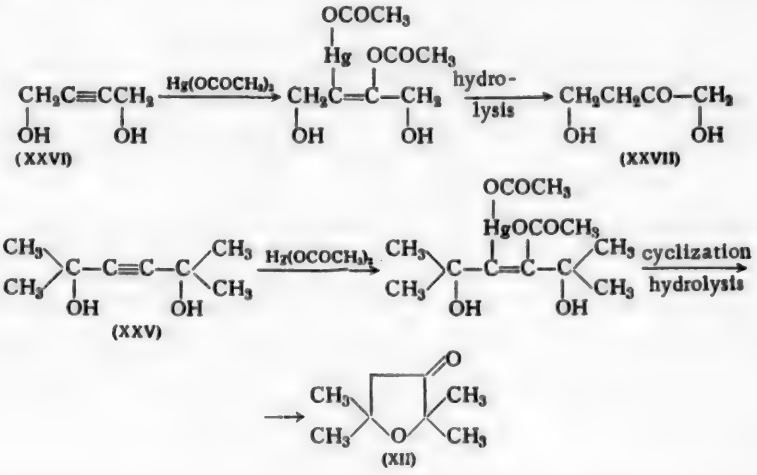
It should be noted that the cyclohydration of acetylenic γ-glycols to tetrahydrofuran-3-ones by the method of Dupont [4] with the help of mercuric sulfate goes with very much greater facility and with a higher yield than cyclization under the same conditions of the corresponding α,β'-ketodiols or unsaturated α-ketoalcohols. Tetramethylbutynediol (XXV), for example, is susceptible to cyclohydration to give a 90% yield of 2,2,5,5-tetrahydrofuran-3-one (XII) even in presence of mercuric acetate, whereas its corresponding ketodiol (VIII) or unsaturated α-ketoalcohol (VII) is not cyclized at all under the same conditions and is recovered unchanged; cyclization only takes place in presence of mercuric sulfate (see table).

According to earlier literature, 2-keto-1,4-diols or unsaturated α-ketoalcohols are intermediates in the formation of tetrahydrofuran-3-ones during hydration of acetylenic γ-glycols in presence of mercuric salts. Our experimental results, however, do not support this mechanism and give grounds for suggesting that cyclohydration of acetylenic γ-glycols to the corresponding furanones goes via organomercury adducts. Mercuric salts apparently add on at the triple bond of acetylenic γ-glycols to form active adducts which are readily transformed into tetra-

hydrofuran-3-ones on cyclization and hydrolysis.



The mercuric adducts of the acetylenic γ-glycols, in dependence on the nature of the substitution at the hydroxyl-containing carbon, can undergo hydrolysis to the corresponding ketodiols or unsaturated α-ketoalcohols without preliminary cyclization. For example, the hydration of butynediol (XXVI) in presence of mercuric acetate leads to formation of only the ketodiol (XXVII) whereas under the same conditions tetramethylbutynediol (XXV) gives the furanone (XII).



A separate communication will be devoted to a detailed examination of the mechanism of hydration of acetylenic γ-glycols, and of cyclization of α,β'-ketodiols and unsaturated α-ketoalcohols to tetrahydrofuran--3-ones.

EXPERIMENTAL

Hydration of dimethylcrotonyl carbinol (I). A mixture of 16 g of α-ketoalcohol (I) (b.p. 66-67° at 10 mm; n_D^{20} 1.4590 [1]) and 80 g of 15% sulfuric acid was vigorously stirred for 15 hours at 50-65°. After cooling, the reaction mass was saturated with potassium carbonate, and the product was carefully extracted with ether, dried with magnesium sulfate, and fractionated in vacuo. 4 g of the original α-ketoalcohol (I) was obtained with b.p. 66-68° (10 mm), n_D^{20} 1.4585; also 9.5 g of dimethyl-β-hydroxybutyryl carbinol (IV). B. p. 113-115° (10 mm), 82-83° (1 mm), n_D^{20} 1.4515 [1].

The semicarbazone of ketodiol (IV) melted at 146-148°.

Found %: N 20.80, 20.72. $C_8H_{17}O_3N_3$. Calculated %: N 20.68.

Dehydration of dimethyl-β-hydroxybutyryl carbinol (IV). 2 g of ketodiol (IV) was distilled in presence of anhydrous potassium bisulfate in vacuo (18 mm) on a metal bath at 125-135°. Fractionation of the distillate gave 1.5 g of dimethylcrotonyl carbinol (I) with b.p. 66-68° (10 mm); n_D^{20} 1.4595.

Acetylation of dimethyl-β-hydroxybutyryl carbinol (IV). To 4.5 g of ketodiol (IV) was added (dropwise), with iced water cooling, 10 g of acetic anhydride containing a trace of sulfuric acid. The reaction mixture was heated on a water bath at 40-45° for 1 hour. The product was diluted with water, neutralized with sodium bicarbonate, extracted with ether and fractionated in vacuo. 5.5 g of dimethyl-β-hydroxybutyryl carbinol diacetate was obtained; b.p. 102-103° (2 mm); n_D^{20} 1.4395 [1].

Cyclization of dimethylcrotonyl carbinol (I). A mixture of 12 g of carbinol (I), 45 g of 15% sulfuric acid and 2 g of mercuric sulfate was heated with vigorous stirring on a water bath at 60-70° for 3 hours. Addition was then made of another 1 g of mercuric sulfate, and heating on the boiling water bath was continued for 7 hours. The product was isolated from the reaction mass by distillation in steam. The distillate was saturated with potassium carbonate and carefully extracted with ether; the ethereal extract was dried with magnesium sulfate and fractionated at atmospheric pressure to give 9 g of 2,2,5-trimethyltetrahydrofuran-3-one (IX) as a colorless, mobile liquid with an odor of camphor.

B. p. 138-140° (677 mm), 37-39° (10 mm), n_D^{20} 1.4225, d_4^{20} 0.9501, MR 34.29; calc. 33.98.

Found %: C 65.62, 65.71; H 9.63, 9.87. $C_7H_{12}O_2$. Calculated %: C 65.59; H 9.43.

The 2,4-dinitrophenylhydrazone of furanone (IX) melted at 105-106° (from alcohol).

Found %: N 18.32, 18.25. $C_{13}H_{16}O_8N_4$. Calculated %: N 18.18.

The semicarbazone melted at 170-171° (from alcohol).

Cyclization of dimethyl-β-hydroxybutyryl carbinol (IV). A mixture of 4 g of the ketodiol (IV), 20 ml of 15% sulfuric acid and 1.5 g of mercuric sulfate was vigorously stirred at 60-80° for 6 hours, and the product was distilled off in steam. The distillate was worked up as described above to give 2.9 g of trimethyltetrahydrofuran-3-one (IX) with b.p. 37-39° (10 mm), n_D^{20} 1.4225; the semicarbazone melted at 170-171° and the melting point was not depressed in admixture with the specimen described above.

Hydrolysis of β-methoxyketol (XXIII) and α-acetoxyketone (XXIV) in presence of mercuric sulfate. a) A mixture of 15 g of dimethyl-β-methoxybutyryl carbinol (XXIII) [1], 50 g of 15% sulfuric acid and 3 g of mercuric sulfate was vigorously stirred at 60-90° for 8 hours. The reaction mass was worked up as described above to give 9 g of furanone (IX) with b.p. 36-39° (10 mm), n_D^{20} 1.4223; the semicarbazone melted at 170-171°.

b) A mixture of 30 g of the acetate of dimethylcrotonyl carbinol (XXIV) [1], 150 g of 15% sulfuric acid and 10 g of mercuric sulfate was vigorously stirred on a boiling water bath for 8 hours until the oily layer had dissolved. After working up in the usual manner, 16 g of furanone (IX) was obtained; b.p. 36-37° (10 mm), n_D^{20} 1.4225; m.p. of semicarbazone 170-171°.

Hydration of methylethylcrotonyl carbinol (II). A mixture of 10 g of α-ketoalcohol (II) (b.p. 74-75° at 10 mm, n_D^{20} 1.4595) [1] and 50 ml of 15% sulfuric acid was vigorously stirred for 17 hours at 50-60°. The reaction mixture was worked up as described above to give 3 g of original compound (II) with b.p. 72-75° (10 mm), n_D^{20} 1.4590, and 5.5 g of methylethyl-β-hydroxybutyryl carbinol (V) in the form of a colorless liquid.

B. p. 91-92° (2.5 mm), 117-118° (9.5 mm), n_D^{20} 1.4532, d_4^{20} 1.0293, MR 42.08; calc. 42.20.

Found %: C 59.88, 59.79; H 10.18, 10.10. $C_8H_{16}O_2$. Calculated %: C 59.97; H 10.06.

Cyclization of methylethylcrotonyl carbinol (II). A mixture of 13 g of α-ketoalcohol (II), 65 g of 15% sulfuric acid and 4 g of mercuric sulfate was vigorously stirred for 8 hours at 60-80°. The product was distilled off from the reaction mass in steam. The distillate was worked up in the usual manner to give 9.5 g of 2,5-dimethyl-2-ethyltetrahydrofuran-3-one (X).

B. p. 50-51° (10 mm), 155-157° (677 mm), n_D^{20} 1.4290, d_4^{20} 0.9461, MR 38.72; calc. 38.59.

Found %: C 67.19, 67.38; H 10.41, 10.10. $C_8H_{14}O_2$. Calculated %: C 67.56; H 9.93.

The semicarbazone of furanone (X) melted at 115-116.5° (from alcohol).

Found %: N 21.38; 21.20. $C_9H_{19}O_2N_3$. Calculated %: N 21.10.

Cyclization of methylethyl-β-hydroxybutyryl carbinol (V). A mixture of 3 g of ketodiol (V), 20 ml of 15% sulfuric acid and 1 g of mercuric sulfate was vigorously stirred at 60-80° for 7 hours. Further treatment was as described above. 1.9 g of 2,5-dimethyl-2-ethyltetrahydrofuran-3-one (X) was obtained; b.p. 50-51° (10 mm), n_D^{20} 1.4290; the semicarbazone melted at 115-116°.

Hydration of methyl-n-propylcrotonyl carbinol (III). A mixture of 5 g of α-ketoalcohol (III) (b.p. 83-85° at 10 mm, n_D^{20} 1.4605) [1] and 25 ml of 15% sulfuric acid was vigorously stirred for 15 hours at 50-65°. The product was worked up in the usual manner to give 2.5 g of the original α-ketoalcohol (III) and 1.6 g of methyl-n-propyl-β-hydroxybutyryl carbinol (VI).

B. p. 94-96° (3 mm), n_D^{20} 1.4545, d_4^{20} 1.0115, MR 46.68; calc. 46.82.

Found %: C 62.22, 62.18; H 10.31, 10.25. $C_9H_{18}O_3$. Calculated %: C 62.04; H 10.41.

Cyclization of methyl-n-propylcrotonyl carbinol (III). A mixture of 4.5 g of α-ketol (III), 20 g of 10% sulfuric acid, 1.5 g of mercuric sulfate and 15 ml of alcohol was stirred at 60-75° for 7 hours. The alcohol was distilled off and the residue distilled in steam. The distillate was worked up in the usual manner to give 2.8 g of 2,5-dimethyl-2-n-propyltetrahydrofuran-3-one (XI).

B. p. 63-65° (10 mm), n_D^{20} 1.4332, d_4^{20} 0.9387, MR 43.24; calc. 43.20.

Found %: C 68.85; 68.95; H 10.24, 10.20. $C_9H_{16}O_2$. Calculated %: C 69.19; H 10.32.

The semicarbazone of furanone (XI) melted at 146-148° (from alcohol).

Found %: N 19.87, 19.88. $C_{10}H_{19}O_2N_3$. Calculated %: N 19.71.

Hydration of 2,5-dimethyl-4-hexen-2-ol-3-one (VII). A mixture of 10 g of α-ketoalcohol (VII) (b.p. 74-75° at 10 mm, n_D^{20} 1.4650) [1] and 40 g of 10% sulfuric acid was vigorously stirred at 50-70° for 15 hours. The mass was worked up in the usual manner to give 6 g of original α-ketoalcohol (VII) and 3 g of 2,5-dimethyl-3-hexanone-2,5-diol (VIII) in the form of a viscous, colorless liquid.

B. p. 72-74° (1 mm), n_D^{20} 1.4445, d_4^{20} 1.0003, MR 42.58; calc. 42.20.

Found %: C 59.82, 59.88; H 10.29, 10.18. $C_8H_{14}O_2$. Calculated %: C 59.97; H 10.06.

The semicarbazone of ketodiol (VIII) melted at 137-139°.

Found %: N 19.06, 19.19. $C_9H_{17}O_2N_3$. Calculated %: N 19.35.

Dehydration of 2,5-dimethyl-3-hexanone-2,5-diol (VIII). 2 g of ketodiol (VIII) was heated in presence of p-toluenesulfonic acid on a boiling water bath for 0.5 hour, after which the product was distilled in vacuo to give 1.2 g of 2,5-dimethyl-4-hexen-2-ol-3-one (VII) with b.p. 73-75° (10 mm), n_D^{20} 1.4650.

Cyclization of 2,5-dimethyl-4-hexen-2-ol-3-one (VII). A mixture of 14 g of the unsaturated ketoalcohol (VII), 50 g of 10% sulfuric acid and 3.5 g of mercuric sulfate was vigorously stirred at 60-80° for 7 hours. The product was distilled off from the reaction mass in steam and worked up in the usual manner to give 11.2 g of 2,2,5,5-tetramethyltetrahydrofuran-3-one (XII) with b.p. 42-43° (11 mm), 143-145° (677 mm), n_D^{20} 1.4212. The semicarbazone melted at 189-190° and did not give a depression in admixture with an authentic specimen [4].

Cyclization of 2,5-dimethyl-3-hexanone-2,5-diol (VIII). A mixture of 2.5 g of ketodiol (VIII), 10 g of 15% sulfuric acid and 1 g of mercuric sulfate was stirred at 70-80° for 5 hours. The mass was worked up as in the previous experiment to give 1.9 g of furanone (XII) with b.p. 42-43° (11 mm), n_D^{20} 1.4215. The semicarbazone melted at 189-190° [4].

Cyclohydration of tetramethylbutynediol (XXV). a) A mixture of 2.5 g of tetramethylbutynediol (XXV), 10 g of 15% sulfuric acid and 1 g of mercuric sulfate was stirred at 70-80° for 0.5 hour. The product was worked up as previously to give 2.45 g of furanone (XII) with b.p. 42-43° (11 mm), n_D^{20} 1.4215. The semicarbazone melted at 188-190° [4].

b) A mixture of 3.5 g of tetramethylbutynediol (XXV), 30 ml of water and 1.5 g of mercuric acetate was refluxed for 3 hours. The reaction mass was saturated with potassium carbonate and the product was extracted with ether, dried with magnesium sulfate and fractionated in vacuo. 3.1 g of furanone (XII) was obtained; b.p. 49-51°

(18 mm); n_D^{20} 1.4210. The semicarbazone melted at 190° and did not give a depression with an authentic specimen.

Under similar reaction conditions (in presence of mercuric acetate), neither 2,5-dimethyl-3-hexanon-2,5--diol (VIII) nor 2,5-dimethyl-4-hexen-2-ol-3-one (VII) are cyclized, and they are recovered unchanged.

Hydration of butynediol (XXVI). A mixture of 40 g of 30% aqueous butynediol (XXVI) solution and 3 g of mercuric acetate was refluxed for 5 hours. The water was distilled off from the reaction mixture on a water bath in vacuo at 30-40°, and the residue was twice distilled in the vacuum of an oil pump to give 7.8 g (55%) of 2--butanone-1,4-diol (XXVII).

B.p. 104-105° (1.5 mm), n_D^{20} 1.4745, d_4^{20} 1.2055, MR 24.40; calc. 23.73.

Found %: C 46.64, 46.67; H 7.23, 7.35. $C_4H_8O_3$. Calculated %: C 46.15; H 7.69.

The ketodiol (XXVII) is a colorless, viscous liquid, readily soluble in water and poorly soluble in ether.

Acetylation of 2-butanone-1,4-diol (XXVII). A drop of sulfuric acid was added to 10 g of acetic anhydride, followed by 5 g of ketodiol (XXVII) while cooling with ice water. The next day, after the usual treatment, 5.5 g of the diacetate of 2-butanone-1,4-diol was obtained; b.p. 115-118° (2.5 mm), n_D^{20} 1.440 [1].

Cyclization of 1-crotonylcyclohexan-1-ol (XIII). A mixture of 8 g of α-ketol (XIII) (b.p. 114-116° at 10 mm, n_D^{20} 1.4960) [1], 40 g of 15% sulfuric acid, 4 g of mercuric sulfate and 35 ml of alcohol was refluxed for 8 hours. The alcohol was distilled off and the residue distilled in steam. The distillate was worked up in the usual fashion to give 5 g of 2,2-pentamethylene-5-methyltetrahydrofuran-3-one (XV).

B. p. 54-55° (1.4 mm), 90-92° (10 mm), n_D^{20} 1.4685, d_4^{20} 1.0190, MR 45.93; calc. 45.63.

Found %: C 70.70, 70.98; H 9.58, 9.60. $C_{10}H_{16}O_2$. Calculated %: C 71.40; H 9.59.

The semicarbazone of furanone (XV) melted at 199-201° (from alcohol).

Found %: N 18.58, 18.60. $C_{11}H_{19}O_2N_3$. Calculated %: N 18.66.

Cyclization of 3,6-dimethyl-5-octen-3-ol-4-one (XIV). A mixture of 6 g of α-ketoalcohol (XIV) (b.p. 94-96° at 10 mm, n_D^{20} 1.4640) [1], 30 ml of 15% sulfuric acid, 25 ml of alcohol and 2.5 g of mercuric sulfate was refluxed for 8 hours. The mass was worked up as before to give 4.2 g of 2,5-dimethyl-2,5-diethyltetrahydrofuran-3-one (XVI) with b.p. 72-74° (10.5 mm), n_D^{20} 1.4378; the semicarbazone melted at 136-138° [4].

Preparation of the unsaturated α-ketoalcohols (XVII and XVIII). 2-Methyl-5-phenyl-4-penten-2-ol-3-one (XVII) was prepared by a modification of the method of Scheibler and Fischer [3] by condensation of dimethylacetyl carbinol with benzaldehyde; b.p. 122-125° (2 mm), n_D^{20} 1.5805; b.p. 38-40°; the 2,4-dinitrophenylhydrazone melted at 141-143° (from alcohol).

Found %: N 14.88, 14.79. $C_{18}H_{18}O_5N_4$. Calculated %: N 15.13.

The acetate of 2-methyl-4-phenyl-4-penten-2-ol-3-one was prepared by the action of acetic anhydride on the α-ketoalcohol (XVII) in presence of sulfuric acid; m.p. 84-85° [3]; the 2,4-dinitrophenylhydrazone melted at 166-168° (from a mixture of alcohol and ethyl acetate).

Found %: N 13.73, 13.58. $C_{20}H_{20}O_6N_4$. Calculated %: N 13.59.

3-Methyl-6-phenyl-5-hexen-3-ol-4-one (XVIII). To a mixture of 13 g of methylethylacetyl carbinol, 12 g of freshly distilled benzaldehyde and 15 ml of methanol was added 5 g of metallic sodium in 100 ml of methanol. The mixture was left for 24 hours at room temperature and then stirred at 50-60° for 3 hours. The methanol was distilled off in a low vacuum, and the product was treated with water and extracted with ether; the extract was dried with magnesium sulfate and fractionally distilled in vacuo to give 18 g of α-ketoalcohol (XVIII) in the form of a yellow viscous oil, b.p. 124-126° (1.5 mm), n_D^{20} 1.5740.

Found %: C 76.61, 76.96; H 7.95, 8.07. $C_{13}H_{16}O_2$. Calculated %: C 76.47; H 7.84.

The 2,4-dinitrophenylhydrazone of the α-ketoalcohol (XVIII) melted at 193-195° (from ethyl acetate).

Found %: N 14.02, 14.25. $C_{19}H_{20}O_5N_4$. Calculated %: N 14.58.

Cyclization of 2-methyl-5-phenyl-4-penten-2-ol-3-one (XVII). A mixture of 10 g of α-ketoalcohol (XVII), 30 ml of 15% sufluric acid, 40 ml of alcohol and 3 g of mercuric sulfate was refluxed for 12 hours. After the alco-

hol had been distilled off, the residue was extracted with ether; the extract was washed with potassium carbonate solution, dried with magnesium sulfate and fractionated in vacuo to give 8 g of 2,2-dimethyl-5-phenyltetrahydrofuran-3-one (XIX) with b.p. 125-128° (10 mm), n_D^{20} 1.5150 [5].

The 2,4-dinitrophenylhydrazone of the furanone (XIX) melted at 166-168° (from ethyl acetate).

Found %: N 15.10, 15.43. $C_{18}H_{18}O_5N_4$. Calculated %: N 15.13.

Cyclization of 3-methyl-6-phenyl-5-hexen-3-ol-4-one (XVIII). A mixture of 9 g of α-ketoalcohol (XVIII), 25 ml of 15% sulfuric acid, 50 ml of ethanol and 3 g of mercuric sulfate was refluxed for 12 hours. The mass was worked up as previously. 7.5 g of 2-methyl-2-ethyl-5-phenyltetrahydrofuran-3-one (XX) was obtained.

B. p. 102-104° (1.5 mm), 141-143° (11.5 mm), n_D^{20} 1.5150, d_4^{20} 1.0526, MR 58.50; calc. 58.09.

Found %: C 76.74, 77.07; H 8.05, 7.99. $C_{13}H_{16}O_2$. Calculated %: C 76.47; H 7.84.

The 2,4-dinitrophenylhydrazone of the furanone (XX) melted at 133-135° (from a mixture of alcohol and ethyl acetate).

Found %: N 14.31, 14.53. $C_{19}H_{20}O_5N_4$. Calculated %: N 14.58.

Preparation of 2,5,6-trimethyl-4-hepten-2,6-diol-3-one (XXI). A mixture of 50 g of dimethylacetyl carbinol and 10 g of finely pulverized, anhydrous potassium carbonate was refluxed for 10 hours. The product of reaction was decanted off and fractionated in vacuo to give 26 g of original dimethylacetyl carbinol and 21 g of unsaturated ketoglycol (XXI) with b.p. 105-108° (9 mm), m.p. 81-82° (from benzene) [6].

Cyclization of 2,5,6-trimethyl-4-hepten-2,6-diol-3-one (XXI). A mixture of 17 g of unsaturated ketoglycol (XXI), 40 ml of 10% sulfuric acid, 45 ml of alcohol and 3 g of mercuric sulfate was refluxed for 10 hours. The reaction mass darkened considerably. After the alcohol had been taken off in a low vacuum, the residue was extracted with ether, the extract was washed with potassium carbonate, dried with magnesium sulfate, and fractionated in vacuo. 3.1 g of 2,2,5-trimethyl-5-isopropenyltetrahydrofuran-3-one (XXII) was obtained.

B. p. 71-73° (9 mm), n_D^{20} 1.4515, d_4^{20} 0.9436, MR 48.01; calc. 47.37.

Found %: C 71.37, 71.38; H 9.68, 9.80. $C_{10}H_{16}O_2$. Calculated %: C 71.44; H 9.52.

The semicarbazone of furanone (XXII) melted at 175-177° (from alcohol).

Found %: N 18.45, 18.36. $C_{11}H_{19}O_2N_3$. Calculated %: N 18.66.

SUMMARY

1. When heated with dilute sulfuric acid (in the absence of mercuric sulfate), aliphatic unsaturated α--ketoalcohols gave only 2-keto-1,4-diols and tetrahydrofuran-3-ones were not formed at all.

2. Heating of unsaturated α-ketoalcohols or 2-keto-1,4-diols with dilute sulfuric acid in presence of mercuric sulfate led to formation of the corresponding tetrahydrofuran-3-ones in good yield.

3. The important role of mercury salts in the cyclization of 2-keto-1,4-diols to the corresponding tetrahydrofuran-3-ones was established.

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189. SYNTHESIS AND TRANSFORMATIONS OF 3-VINYLETHYNYLTETRAHYDROFURAN-3-OLS

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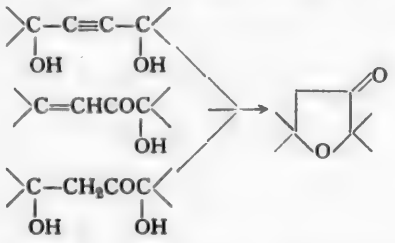
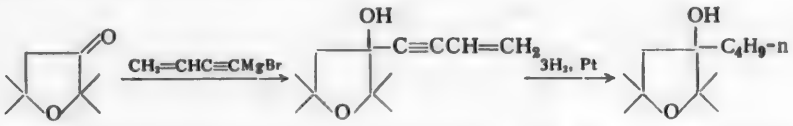
In our laboratory we earlier made a detailed study of the transformations of diverse vinylethynyl carbinols [1], but vinylethynyl carbinols of the tetrahydrofuran series were excluded from the work. It appeared to us necessary to fill this gap and to effect the synthesis of 3-vinylethynyltetrahydrofuran-3-ols from tetrahydrofuran-3-ones which are easily obtained by hydration of acetylenic γ-glycols by the Dupont method [2], and also by cyclization of unsaturated α-ketoalcohols or ketodiols, as we previously described [3].

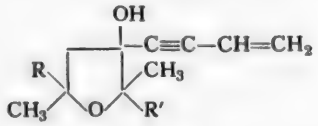


Attempts to condense vinylacetylene with tetrahydrofuran-3-ones in presence of pulverized potassium hydroxide remained unsuccessful. This failure is apparently due to formation of the potassium alcoholate of the enol form of the furanone, which hinders further reaction. It is well known that some furanones react with a Grignard reagent only in the enol form, and enolates are formed by the action of potassium hydroxide. [2].

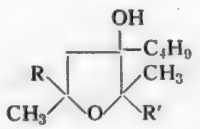
We effected the synthesis of 3-vinylethynyltetrahydrofuran-3-ols in a yield of about 90% by reacting vinylethynyl magnesium bromide with tetrahydrofuran-3-ones.



In this manner we prepared the 3-vinylethynyltetrahydrofuran-3-ols (I-V) which on hydrolysis with Pt catalyst absorbed 3 moles of hydrogen to form the corresponding 3-butyltetrahydrofuran-3-ols (VI-X).



(I) R=H, R′=CH₃,
(II) R=R′=CH₃,
(III) R=H, R′=C₂H₅,
(IV) R=R′=C₂H₅,
(V) R=R′=(CH₂)₅

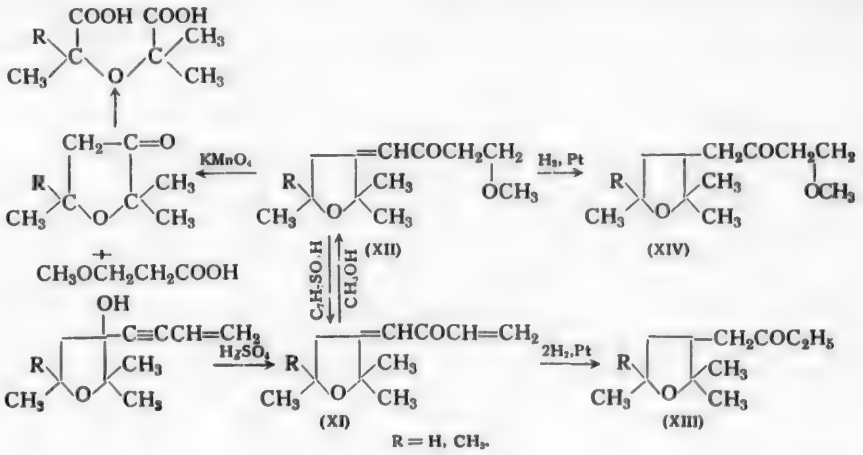


(VI) R=H, R′=CH₃,
(VII) R=R′=CH₃,
(VIII) R=H, R′=C₂H₅,
(IX) R=R′=C₂H₅,
(X) R=R′=(CH₂)₅

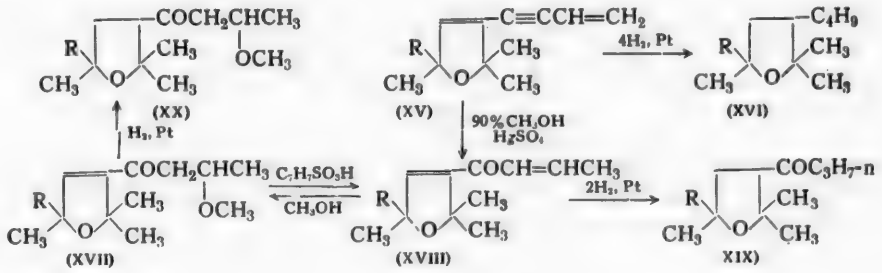
* Deceased.

3-Vinylethynyl-2,2,5-trimethyltetrahydrofuran-3-ol (I) and 3-vinylethynyl-2,2,5,5-tetramethyltetrahydrofuran-3-ol (II) were used as starting substances in a study of some transformations of our vinylacetylenic furanols. Vinylethynyltetrahydrofuranols (I) and (II), like other vinylethynyl carbinols, undergo isomerization when heated in anhydrous methanol solution in presence of mercuric acetate and form dienones (XI) which, under the experimental conditions, add on 1 molecule of methanol and give methoxyketones (XII). The structure of the methoxyketone (XII, R = CH_3) was verified by oxidation with potassium permanganate which gave β-methoxybutyric acid and 2,2,5,5-tetramethyltetrahydrofuran-3-one; under the experimental conditions, the latter is further oxidized to tetramethyldiglycolic acid [2].

Distillation of methoxyketones (XII) in presence of p-toluenesulfonic acid leads to cleavage of methanol with formation of the original dienones which on hydrogenation in presence of Pt catalyst take up two molecules of hydrogen and give saturated ketones (XIII). Hydrogenation of methoxyketones (XII) in presence of Pt catalyst, after absorption of 1 molecule of hydrogen, leads to formation of the corresponding saturated methoxyketones (XIV).



Distillation of vinylethynyltetrahydrofuranols (I) and (II) over potassium bisulfate results in dehydration to the corresponding dienynes (XV). On hydrogenation in alcoholic solutions in presence of Pt catalyst, the dienynes take up 4 molecules of hydrogen and give the corresponding 3-butyltetrahydrofurans (XVI). As was to be expected, the above-metnioned dienynes (XV) are smoothly hydrated on heating in aqueous methanol in presence of mercuric sulfate to form the corresponding methoxyketones (XVII). When heated with p-toluenesulfonic acid they form the dienones (XVIII), which in presence of Pt catalyst absorb 2 molecules of hydrogen and give the saturated ketones (XIX). Under similar conditions of hydrogenation, the unsaturated methoxyketones (XVII) are converted into the saturated methoxyketones (XX).



EXPERIMENTAL

Preparation of 2,2,5-trimethyl-3-vinylethynyltetrahydrofuran-3-ol (I). A Grignard reagent was prepared in a three-necked flask, fitted with mechanical stirrer, reflux condenser and dropping funnel, from 16 g of magnesium turnings, 90 g of ethyl bromide, and 500 ml of absolute ether. Addition was then made, with continuous stirring

at −5°, of about 100 ml of vinylacetylene. The following day the reaction mixture was stirred at the boiling point of ether until ethane ceased to come off; dropwise addition was then made at −12° of 65 g of 2,2,5-trimethyltetrahydrofuran-3-one [3].

After being stirred for 2 hours at room temperature and for 4 hours at the boiling point of ether, the reaction mixture was hydrolyzed with 8% hydrochloric acid. The ethereal layer was neutralized with sodium carbonate, washed with water and dried with magnesium sulfate. After removal of the ether, the residue was distilled in vacuo to give 81.5 g of 2,2,5-trimethyl-3-vinylethynyltetrahydrofuran-3-ol (I).

B. p. 78-79° (1.5 mm), n_D^{20} 1.5000, d_4^{20} 1.0029. MR 52.87; calc. 51.50.

Found %: C 73.42, 73.35; H 9.35, 9.53. $C_{11}H_{16}O_2$. Calculated %: C 73.31; H 8.95.

After standing for 2 months in a closed flask, the carbinol polymerized to a colorless, transparent jelly.

Hydrogenation of 2,2,5-trimethyl-3-vinylethynyltetrahydrofuran-3-ol (I). 4.4 g of freshly distilled crbinol (I) was hydrogenated in solution in 10 ml of alcohol in presence of Pt catalyst. 1.75 liters of hydrogen was taken up (the calculated amount was 1.70 liters). Fractionation in vacuo gave 4 g of 2,2,5-trimethyl-3-butyltetrahydrofuran-3-ol (VI).

B. p. 97-98° (11 mm), n_D^{20} 1.4515, d_4^{20} 0.9194, MR 54.58; calc. 53.97.

Found %: C 71.19, 71.05; H 12.43, 12.02. $C_{11}H_{22}O_2$. Calculated %: C 70.96; H 11.82.

Preparation of 2,2,5,5-tetramethyl-3-vinylethynyltetrahydrofuran-3-ol (II). To a solution of ethyl magnesium bromide, prepared from 24 g of magnesium turnings, 110 g of ethyl bromide and 500 ml of absolute ether, was added (cooling at −5°) about 150 ml of vinylacetylene. The following day, after stirring at room temperature for 3 hours, dropwise addition was made (cooling to −10°) of 88 g of 1,1,5,5-tetramethyltetrahydrofuran-3-one [2, 3]. The remainder of the experiment was carried out as described above. Fractional distillation of the product in vacuo gave 87.8 g of 2,2,5,5-tetramethyl-3-vinylethnyltetrahydrofuran-3-ol (II) with b.p. 116-118° (4 mm) in the form of a very viscous liquid which crystallized after standing for a short time; m.p. 52-54° (from ligroine).

Found %: C 74.82, 74.59; H 9.22, 9.18. $C_{12}H_{18}O_2$. Calculated %: C 74.22; H 9.27.

Hydrogenation of 2,2,5,5-tetramethyl-3-vinylethynyltetrahydrofuran-3-ol (II). 2.6 g of recrystallized carbinol (II) was hydrogenated in solution in 10 ml of alcohol in presence of Pt catalyst. The volume of hydrogen taken up was 1.0 liter (as against the theoretical requirement of 0.96 liter). 2.2 g of 2,2,5,5-tetramethyl-3-butyltetrahydrofuran-3-ol (VII) was obtained in the form of a colorless, viscous liquid.

B.p. 111-112° (16 mm), n_D^{20} 1.4564, d_4^{20} 0.9244, MR 58.81; calc. 58.58.

Found %: C 71.57, 71.78; H 12.11, 12.17. $C_{12}H_{24}O_2$. Calculated %: C 72.00; H 12.00.

Preparation of 2,5-dimethyl-2-ethyl-3-vinylethynyltetrahydrofuran-3-ol (III). Vinylethynyl magnesium bromide was prepared, as indicated above, from 2.4 g of magnesium turnings, 12 g of ethyl bromide, 50 ml of absolute ether and 25 ml of vinylacetylene. Dropwise addition was then made (cooling to −4°) of 11.8 g of 2,5-dimethyl-2-ethyltetrahydrofuran-3-one [3]. The reaction product was worked up in the usual manner to give 12 g of 2,5-dimethyl-2-ethyl-3-vinylethynyltetrahydrofuran-3-ol (III).

B.p. 110-111° (5 mm), n_D^{20} 1.5010, d_4^{20} 0.9895, MR 57.76; calc. 56.11.

Found %: C 73.85, 73.91; H 9.46, 9.62. $C_{12}H_{18}O_2$. Calculated %: C 74.22; H 9.27.

Hydrogenation of 2,5-dimethyl-2-ethyl-3-vinylethynyltetrahydrofuran-3-ol (III). Exhaustive hydrogenation of 3.5 g of freshly distilled crabinol (III) in solution in 15 ml of alcohol in presence of Pt catalyst gave 3 g of 2,5-dimethyl-2-ethyl-3-butyltetrahydrofuran-3-ol (VIII).

B. p. 93-94° (5 mm), n_D^{20} 1.4568, d_4^{20} 0.9309, MR 58.52; calc. 58.58.

Found %: C 71.58, 71.81; H 12.11, 12.21. $C_{12}H_{24}O_2$. Calculated %: C 72.00; H 12.00.

Preparation of 2,5-dimethyl-2,5-diethyl-3-vinylethynyltetrahydrofuran-3-ol (IV). To vinylethynyl magnesium bromide, prepared from 2 g of magnesium turnings, 10 g of ethyl bromide, 50 ml of absolute ether and 25 ml of vinylacetylene, was added (dropwise with cooling) 12 g of 2,5-dimethyl-2,5-diethyltetrahydrofuran-3-one

[2, 3]. The reaction mass was worked up in the usual fashion to give 8 g of 2,5-dimethyl-2,5-diethyl-3-vinylethynyl-tetrahydrofuran-3-ol (VI).

B. p. 102-103° (2 mm), n_D^{20} 1.5020, d_4^{20} 0.9596, MR 68.27; calc. 65.35.

Found %: C 75.79, 75.70; H 9.95, 10.05. $C_{14}H_{22}O_2$. Calculated %: C 75.63; H 9.95.

Hydrogenation of 2,5-dimethyl-2,5-diethyl-3-vinylethynyltetrahydrofuran-3-ol (IV). Exhaustive hydrogenation of 3.2 g of carbinol (IV) in solution in 15 ml of alcohol in presence of Pt catalyst gave 2.8 g of 2,5-dimethyl-2,5--diethyl-3-butyltetrahydrofuran-3-ol (IX).

B. p. 97° (3 mm), n_D^{20} 1.4585, d_4^{20} 0.9117, MR 68.22; calc. 67.82.

Found %: C 73.65, 73.72; H 12.66, 12.91. $C_{14}H_{28}O_2$. Calculated %: C 73.69; H 13.05.

Preparation of 2,5-bispentamethylene-3-vinylethynyltetrahydrofuran-3-ol (V). 10 g of 2,5-bispentamethyl-enetetrahydrofuran-3-one [2] was added to vinylethynyl magnesium bromide prepared from 2 g of magnesium turnings, 10 g of ethyl bromide, 50 ml of absolute ether and 25 ml of vinylacetylene. After the mass had been worked up in the usual fashion and the ether had been removed, the solid residue was recrystallized from ligroine to give 6 g of 2,5-bispentamethylene-3-vinylethynyltetrahydrofuran-3-ol (V) with m.p. 103-104°.

Found %: C 78.63, 78.75; H 9.56, 9.61. $C_{18}H_{26}O_2$. Calculated %: C 78.90; H 9.49.

Hydrogenation of 2,5-bispentamethylene-3-vinylethynyltetrahydrofuran-3-ol (V). Exhaustive hydrogenation of 3 g of carbinol (V) in solution in 15 ml of alcohol in presence of Pt catalyst gave 2.5 g of 2,5-bispentamethylene--3-butyltetrahydrofuran-3-ol (X) in the form of a colorless, viscous liquid with b.p. 164° (3 mm), n_D^{20} 1.4965.

Found %: C 76.53, 76.82; H 11.68, 11.51. $C_{18}H_{32}O_2$. Calculated %: C 77.14; H 11.33.

Isomerization of 2,2,5,5-tetramethyl-3-vinylethynyltetrahydrofuran-3-ol (II). A mixture of 20.7 g of recrystallized carbinol (II), 80 g of methanol and 4 g of mercuric sulfate (added in small portions) was stirred on a water bath at 60-70° for 7 hours. The reaction product was decanted from the catalyst, the main bulk of the methanol was distilled off in a low vacuum, and the residue was neturalized with potassium crabonate, extracted with ether, and dried with magnesium sulfate. Yield 16 g of methoxyketone (XII, R = CH_3).

B. p. 95-96° (2 mm), n_D^{20} 1.4600, d_4^{20} 0.9731, MR 63.63; calc. 62.86.

Found %: C 68.81, 68.98; H 10.01, 10.05. $C_{13}H_{22}O_3$. Calculated %: C 69.02; H 9.73.

Hydrogenation of the methoxyketone (XII, R = CH_3). 3 g of methoxyketone (XII, R = CH_3) in solution in 10 ml of alcohol was hydrogenated in presence of Pt catalyst. 0.4 liter of hydrogen was absorbed (the theoretical requirment is 0.31 liter). There was obtained 2.3 g of saturated methoxyketone (XIV; R = CH_3).

B. p. 85-86° (2 mm), n_D^{20} 1.4514, d_4^{20} 0.9643, MR 63.64; calc. 63.33.

Found %: C 67.82, 68.08; H 10.53, 10.62. $C_{13}H_{24}O_3$. Calculated %: C 68.42; H 10.52.

The 2,4-dinitrophenylhydrazone of the methoxyketone (XIV, R = CH_3) melted at 163-165° (from alcohol).

Oxidation of methoxyketone (XII, R = CH_3). 21 g of finely pulverized potassium permanganate was introduced in small portions in the course of 6 hours into a mixture of 10.8 g of methoxyketone (XII, R = CH_3) and 200 ml of water with vigorous stirring and cooling with ice water. The next day the precipitated manganese dioxide was pressed and washed with 50 ml of hot water. The filtrate was carefully extracted with ether to remove neutral products. After the ether had been removed, a semicarbazone with m.p. 188-190° was obtained from the residue; it did not give a depression of melting point with the semicarbazone of 2,2,5,5-tetramethyltetrahydrofuran-3-one [2, 3]. The filtrate was evaporated to dryness on a water bath, and the residue was acidifted with concentrated hydrochloric acid and extracted with ether; the ethereal extract was dried with magnesium sulfate. The ether was removed to leave 1.3 g of β-methoxypropionic acid with b.p. 103-105° (11 mm), 200-202° (675 mm), n_D^{20} 1.4200; also 1 g of tetramethyldiglycolic acid with m.p. 151-151.5° (from alcohol) [2].

Cleavage of methanol from the methoxyketone (XII, R = CH_3). 6 g of methoxyketone (XII, R = CH_3), 0.005 g of pyrogallol and 0.05 g of p-toluenesulfonic acid were heated on a boiling water bath under a vacuum of 25 mm; the product was then distilled in the vacuum of an oil pump. Redistillation gave 3 g of the dienol (XI, R = CH_3).

B. p. 73-74° (1 mm), n_D^{20} 1.4690, d_4^{20} 0.9461, MR 57.21; calc. 56.13.

Found %: C 72.67, 73.05; H 9.61, 9.43. $C_{12}H_{18}O_2$. Calculated %: C 74.22; H 9.27.

Hydrogenation of the dienol (XI, R = CH_3). 2.8 g of freshly distilled dienol (XI, R = CH_3) in solution in 10 ml of alcohol was hydrogenated in presence of Pt catalyst. 0.7 liter of hydrogen was absorbed (the theoretical requirement is 0.693 liter), and 2.1 g of saturated ketone (XIII, R = CH_3) was obtained.

B. p. 85-86° (5 mm); n_D^{20} 1.449, d_4^{20} 0.9235, MR 57.52; calc. 57.07.

Found %: C 72.25, 72.48; H 10.94, 11.09. $C_{12}H_{22}O_2$. Calculated %: C 72.72; H 11.11.

The 2,4-dinitrophenylhydrazone melted at 140-142° (from alcohol).

Dehydration of 2,2,5,5-tetramethyl-3-vinylethynyltetrahydrofuran-3-ol (II). A mixture of 15 g of carbinol (II), 3.5 g of pulverized, anhydrous potassium bisulfate and 0.005 g of pyrogallol was distilled in vacuo (20 mm) on a metal bath at 100-120°. The product was dried and distilled to give 10 g of 2,2,5,5-tetramethyl-3-vinylethynyl-$\Delta^{3,4}$-dihydrofuran (XV, R = CH_3).

B. p. 83-84° (14 mm), n_D^{20} 1.5018, d_4^{20} 0.8966, MR 57.97; calc. 54.12.

Found %: C 81.49, 81.63; H 9.14, 9.18. $C_{12}H_{16}O_2$. Calculated %: C 81.81; H 9.09.

Hydrogenation of the dienyne (XV, R = CH_3). 2.5 g of freshly distilled substance (XV, R = CH_3) in solution in 10 ml of alcohol was hydrogenated in presence of Pt catalyst. It took up 1.4 liters of hydrogen (instead of the theoretical quantity of 1.36 liters) and gave 2 g of 2,2,5-tetramethyl-3-butyltetrahydrofuran (XVI, R = CH_3).

B. p. 79-80° (15 mm), n_D^{20} 1.4315, d_4^{20} 0.8335, MR 57.10; calc. 57.06.

Found %: C 77.67, 77.89; H 12.92, 13.10. $C_{12}H_{24}O$. Calculated %: C 78.26; H 13.04.

Hydration of the dienyne (XV, R = CH_3) A mixture of 18 g of dienyne (XV, R = CH_3), 80 g of 80% methanol, 2 ml of sulfuric acid and 2 g of mercuric sulfate was stirred at 60-65° for 22 hours. During this operation another 4 g of mercuric sulfate was added in small portions. After the methanol had been distilled off, the residue was neutralized with sodium carbonate solution, extracted with ether, and dried with magnesium sulfate to give 13 g of the dihydrofuranic methoxyketone (XVII, R = CH_3).

B. p. 100-101° (5 mm), n_D^{20} 1.4605, d_4^{20} 0.9571, MR 64.81; calc. 62.85.

Found %: C 69.08, 69.11; H 10.06, 9.95. $C_{13}H_{22}O_3$. Calculated %: C 69.02; H 9.73.

Hydrogenation of the methoxyketone (XVII, R = CH_3). 3.5 g of the compound (XVII, R = CH_3) in solution in 10 ml of alcohol was hydrogenated in presence of Pt catalyst. It took up the theoretical quantity of hydrogen and gave 3 g of the saturated methoxyketone (XX, R = CH_3).

B. p. 110-112° (11 mm), n_D^{20} 1.4424, d_4^{20} 0.9436, MR 63.96; calc. 63.33.

Found %: C 69.12, 68.82; H 11.06, 10.88. $C_{13}H_{24}O_3$. Calculated %: C 68.42; H 10.52.

The 2,4-dinitrophenylhydrazone melted at 113-115° (from alcohol).

Cleavage of methanol from the methoxyketone (XVII, R = CH_3). A mixture of 10 g of methoxyketone (XVII, R = CH_3), 0.05 g of p-toluenesulfonic acid and 0.005 g of pyrogallol was heated in vacuo (6 mm) on a metal bath at 95-105°. Redistillation gave 5 g of dienone (XVIII, R = CH_3).

B. p. 80-81° (2 mm), n_D^{20} 1.4800, d_4^{20} 0.9411, MR 58.55; calc. 56.14.

Found %: C 73.45, 73.81; H 9.77, 9.57. $C_{12}H_{18}O_2$. Calculated %: C 74.22; H 9.27.

Hydrogenation of the dienone (XVIII, R = CH_3). 3.2 g of dienone (XVIII, R = CH_3) in solution in 15 ml of alcohol was hydrogenated in presence of Pt catalyst. 0.8 liter of hydrogen was absorbed (theory requires 0.74 liter). Fractionation in vacuo gave 2.5 g of saturated ketone (XIX, R = CH_3).

B. p. 77-78° (4 mm), n_D^{20} 1.4425, d_4^{20} 0.9069, MR 57.87; calc. 57.07.

Found %: C 72.23, 72.55; H 11.52, 11.31. $C_{12}H_{22}O_2$. Calculated %: C 72.72; H 11.11.

The 2,4-dinitrophenylhydrazone melted at 138-140° (from alcohol).

Isomerization of 2,2,5-trimethyl-3-vinylethynyltetrahydrofuran-3-ol (I, R = H). A mixture of 15 g of carbinol (I, R = H), 75 g of methanol and 3 g of mercuric sulfate (introduced in small protions) was stirred at 55-65° for 7 hours. The material was worked up as described above to give 10.2 g of methoxyketone (XII, R = H).

B. p. 113-114° (5.5 mm), n_D^{20} 1.4710, d_4^{20} 1.0007, MR 59.27; calc. 58.25.

Found %: C 68.16, 68.05; H 9.84, 9.63. $C_{12}H_{20}O_3$. Calculated %: C 67.92; H 9.42.

Hydrogenation of methoxyketone (XII, R = H). 2.7 g of methoxyketone (XII, R = H) in solution in 10 ml of alcohol was hydrogenated in presence of Pt catalyst. The theoretical quantity of hydrogen was absorbed, and 2.2 g of saturated methoxyketone (XIV, R = H) was obtained.

B. p. 97-99° (3 mm), n_D^{20} 1.4500, d_4^{20} 0.9643, MR 59.66; calc. 58.71.

Found %: C 66.90, 67.10; H 10.88, 10.52. $C_{12}H_{22}O_3$. Calculated %: C 67.29; H 10.28.

Cleavage of methanol from methoxyketone (XII, R = H). 8.3 g of methoxyketone (XII, R = H) and 0.05 g of p-toluenesulfonic acid were heated for 30 minutes on a boiling water bath in vacuo (15 mm), after which the product was distilled off in the vacuum of an oil bath to give 4 g of dienone (XI, R = H).

B. p. 85-87° (4 mm), n_D^{20} 1.4800, d_4^{20} 0.9793, MR 52.21; calc. 51.52.

Found %: C 72.58, 72.88; H 9.62, 9.31. $C_{11}H_{16}O_2$. Calculated %: C 73.33; H 8.88.

Dehydration of 2,2,5-trimethyl-3-vinylethynyltetrahydrofuran-3-ol (I, R = H). A mixture of 10 g of carbinol (I), 3 g of anhydrous potassium bisulfate and 0.005 g of pyrogallol was distilled in vacuo (15 mm) on a metal bath at 100-120°. After drying, the distillate was redistilled and gave 6 g of dienyne (XV, R = H).

B. p. 79-80° (15 mm), n_D^{20} 1.5070, d_4^{20} 0.8948, MR 53.88; calc. 49.51.

Found %: C 80.64, 80.88; H 9.14, 8.85. $C_{11}H_{14}O$. Calculated %: C 81.48; H 8.64.

Hydrogenation of dienyne (XV, R = H). 2.7 g of freshly distilled compound (XV, R = H) in solution in 10 ml of alcohol was hydrogenated in presence of Pt catalyst. It absorbed 1.7 liters of hydrogen (theory requires 1.6 liters) and gave 2 g of 2,2,5-trimethyl-3-butyltetrahydrofuran (XVI, R = H).

B. p. 76-77° (12 mm), n_D^{20} 1.4326, d_4^{20} 0.8321, MR 53.11; calc. 52.44.

Found %: C 78.05, 77.82; H 13.11, 13;05. $C_{11}H_{22}O$. Calculated %: C 77.64; H 12.94.

Hydration of the dienyne (XV, R = H). A mixture of 19 g of dienyne (XV, R = H), 70 g of 90% methanol, 1 ml of sulfuric acid and 1 g of mercuric sulfate was stirred at 60-65° for 24 hours. During this period another 6 g of mercuric sulfate was introduced in small portions. The reaction mixture was worked up in the usual fashion to give 15.8 g of methoxyketone (XVII, R = H).

B. p. 94-95° (4 mm), n_D^{20} 1.4660, d_4^{20} 0.9784, MR 60.01; calc. 58.25.

Found %: C 67.90, 67.92; H 10.06, 9.78. $C_{12}H_{20}O_3$. Calculated %: C 67.83; H 9.43.

Hydrogenation of the methoxyketone (XVII, R = H). 3 g of compound (XVII, R = H). in solution in 10 ml of alcohol was hydrogenated in presence of Pt catalyst, absorbing 0.4 liter of hydrogen (instead of the 0.34 liter demanded by theory). 2.5 g of the saturated methoxyketone (XX, R = H) was obtained.

B. p. 85-87° (3 mm), n_D^{20} 1.4468, d_4^{20} 0.9518, MR 60.08; calc. 58.71.

Found %: C 67.26, 67.31; H 10.51, 10.42. $C_{12}H_{22}O_3$. Calculated %: C 67.29; H 10.28.

Cleavage of methanol from the methoxyketone (XVII, R = H). 11 g of the methoxyketone (XVII, R = H) and 0.05 g of p-toluenesulfonic acid were heated on a boiling water bath for 20 minutes in vacuo (12 mm), after which the product was distilled off in the vacuum of an oil pump to give 6 g of dienone (XVIII, R = H).

B. p. 88-90° (5 mm), n_D^{20} 1.4890, d_4^{20} 0.9511, MR 54.46; calc. 51.52.

Found %: C 72.60, 72.88; H 9.42, 9.15. $C_{11}H_{16}O_2$. Calculated %: C 73.33; H 8.88.

Hydrogenation of the dienone (XVIII, R = H). 5.2 g of freshly distilled compound (XVIII, R = H) in solution in 15 ml of alcohol was hydrogenated in presence of Pt catalyst. It absorbed 1.4 liters of hydrogen (instead

of the 1.38 liters demanded by theory) and gave 4.5 g of saturated ketone (XIX, R = H).

B. p. 77-79° (4 mm), n_D^{20} 1.4450, d_4^{20} 0.9249, MR 52.95; calc. 52.45.

Found %: C 71.29, 71.35; H 11.18, 10.95. $C_{11}H_{20}O_2$. Calculated %: C 71.51; H 10.87.

SUMMARY

A series of 3-vinylethynyltetrahydrofuran-3-ols was synthesized and some of their transformations (isomerization, dehydration, hydration of the corresponding dienynes, and hydrogenation) were studied.

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DETERMINATION OF PRIMARY CHLORIDES OF THE ALLYLIC TYPE IN MIXTURES WITH ISOMERIC TERTIARY CHLORIDES

K. V. Leets, A. I. Pilyavskaya and M. I. Korovkina

It is well known that the quantitative determination of isomeric chlorides of the allylic type in their mixtures (obtained on hydrogenation of dienic hydrocarbons [1-3] or on telomerization of the latter with halogenated derivatives [4-6]) with the help of the usual chemical and physicochemical methods is rather inaccurate due to the facility of isomerization of these compounds [4, 7, 8]. All of the more accurate determinations of such mixtures are effected exclusively by the method of comparison of the infrared spectra of the pure isomers and their mixtures [9]. This involves considerable labor and it is not always possible to prepare the corresponding pure isomers.

With the objective of developing a chemical method of quantitative determination of chlorides of the allylic type in their mixtures, we studied the kinetics of reaction of the isomeric products of hydrochlorination of isoprene (1-chloro-3-methylbutene-2 $(CH_3)_2C=CH-CH_2Cl$ (I) and 2-chloro-2-methylbutene-3 $(CH_3)_2CCl-CH=CH_2$ (II)) and of their mixtures with anhydrous KI in acetone.

We used a saturated solution with excess of crystalline KI. On performing the reaction at constant temperature with good stirring, the concentration of one component (KI) in solution remains constant, and the kinetic equation of the reaction acquires the form of the equation of a monomolecular reaction:

$$\log \frac{a_0}{a_0 - a} = kt \qquad (1)$$

where a_0 is the quantity of reacting chloride at 0°, and $\underline{a}$ is the quantity of chloride entering into reaction after a definite time $\underline{t}$.

The quantity of chloride entering into reaction was determined from the quantity of iodide formed. For this purpose the reaction was carried out in presence of hexamethylenetetramine. The latter almost instantaneously forms a salt of the quaternary base with iodides in acetone solution: $[RC_6H_{12}N_4]^+ I^-$.

The quantity of hexamethylenetetramine consumed was determined by titration of the excess of hexamethylenetetramine with hydrochloric acid in presence of formaldehyde, using bromophenol blue as indicator. Under these conditions the excess of hexamethylenetetramine titrates as a monoacidic base, while the salt of the quaternary base does not enter into reaction with acid.

Figure 1 contains kinetic curves of reaction of 1-chloro-3-methylbutene-2 (I), 2-chloro-2-methylbutene-3 (II) and their mixtures (I + II = 1 : 1) with a saturated solution of KI in acetone at 20°.

We see from the diagram that only the primary chloride enters into reaction under the given conditions.

Formation of a small quantity (3.8%) of the salt of the quaternary base with the tertiary isomer is due to the presence in the latter of primary isomer, since here, just as in the case of the primary chloride, the reaction is completed in the course of 2-3 hours (Fig. 1).

For calculation of the velocity constants of the reaction of the primary chloride with KI, the value of a_0 (equation 1) was taken as the quantity of chloride determined after completion of the reaction (horizontal portion of the curves in Fig. 1). The velocity constants calculated for propenyl chloride (1-chloro-3-methylbutene-2) and for its mixture with the tertiary isomer are in good agreement at different stages of the reaction (k = 0.0186-

-0.0193 sec^{-1}). This is also additional evidence that only the primary isomer enters into reaction.

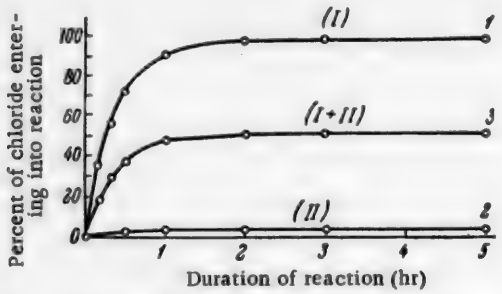

Fig. 1. Kinetics of reaction of isomeric products of hydrochlorination of isoprene with potassium iodide in acetone at 20°
1) 1-chloro-3-methylbutene-2 (I); 2) 2-chloro-2-methylbutene-3 (II); 3) equimolar mixture of (I) and (II).

The method was employed for the purpose of developing a procedure for determination of the content of geranyl chloride in the synthetic product [6]. The corresponding curve is plotted in Fig. 2. The calculated velocity constants are close to the corresponding constants of prenyl chloride (k = 0.0167-0.0174 sec^{-1}).

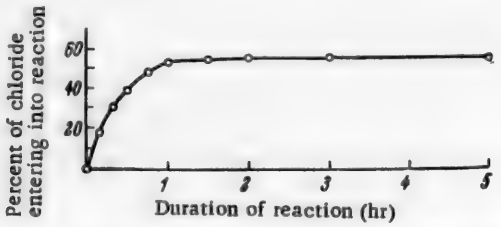

Fig. 2. Kinetics of reaction of geranyl chloride with potassium iodide in a mixture with isomeric terpenic chlorides.

From the corresponding velocity constants we can find the necessary minimum reaction period in the course of which substantially the whole of the primary chloride enters into reaction:

$$\tau = \frac{\log \frac{a_0}{a_0 - a}}{k} = \frac{\log 1000}{k} = \frac{3}{k} \qquad (2)$$

At 20° a value of $\tau = 2^1/_2$ hr was calculated for prenyl chloride, and a value of $\tau = 3$ hr for geranyl chloride. These are in good agreement with the experimental values (see diagrams).

The method opens up extensive possibilities of quantitative study of the hydrohalogenation of dienic hydrocarbons and of the telomerization of these hydrocarbons with halogenated derivatives, as well as of study of the isomerization of allylic halogenated derivatives under the influence of various factors.

EXPERIMENTAL

1. Starting substance. Hexamethylenetetramine, chemically pure grade, was dried to constant weight at 105°.

Formaldehyde was used in the form of a 30% aqueous solution of formaldehyde freed of organic acids. Any acidic impurities (determined by titration with 0.1 N NaOH) were removed by distillation over $CaCO_3$.

Acetone (chemically pure) was dried over anhydrous calcium chloride.

The potassium iodide was "pure for analysis" (GOST standard 4232-48).

1-Chloro-3-methylbutene-2 (I) and 2-chloro-2-methylbutene-3 (II) were prepared by hydrochlorination of isoprene with anhydrous hydrogen chloride in equimolar amounts, followed by fractional distillation of the mixed isomers [8].

(I): b.p. 39-40° (50 mm), d_4^{20} 0.929, n_D^{20} 1.449.

Found %: Cl 33.78. C_5H_9Cl. Calculated %: Cl 33.91.

(II): b.p. 32-34° (120 mm), d_4^{20} 0.887, n_D^{20} 1.419.

Found %: Cl 33.33. C_5H_9Cl. Calculated %: Cl 33.91.

Geranyl chloride (synthetic mixture of terpenic chlorides) was prepared by telomerization of isoprene with the products of its hydrochlorination in presence of anhydrous tin chloride [6].

B. p. 60-90° (2 mm), d_4^{20} 0.936, n_D^{20} 1.478 .

Found %: Cl 20.40. $C_{10}H_{17}Cl$. Calculated %: Cl 20.53.

2. Study of reaction of 1-iodo-3-methylbutene-2 with hexamethylenetetramine in acetone. A weighed quantity of chloride (I) (0.5 g) was put into a 100 ml flask with a ground-glass stopper. The chloride was converted to iodide by adding an excess of KI (2 g and acetone (20 ml). The mixture was shaken at room temperature (20°) for 6 hours. A weighed quantity of hexamethylenetetramine(approx. 1 g) was then introduced, followed after a specified interval of time by 2-3 drops of acetone solution of bromophenol blue (0.1%). The mixture was titrated with 0.5 N aqueous hydrochloric acid until a greenish-yellow color was obtained (see table).

Results of Determinations

Experiment number	Weight of sample in g		Period of reaction (min)	0.5 N HCl consumed in titration of excess of hexamethylenediamine		Quantity of hexamethylenediamine entering into reaction (mmole)	Molar ratio of $[R\ hexa]^+I^-$ to chloride
	chloride	hexamethylenetetramine		(ml)	(mmoles)		
1	0.5368	0.9831	2	4.00	2.00	5.013	0.9766 : 1
2	0.4891	0.9266	10	2.07	1.035	4.575	0.9782 : 1
3	0.6263	1.0269	30	2.91	1.455	5.870	0.9802 : 1
4	0.5891	1.0345	60	3.74	1.87	5.509	0.9780 : 1
5	0.6002	0.9760	120	2.66	1.33	5.627	0.9805 : 1

3. Study of kinetics of reaction of KI with the isomeric chlorides and their mixture in acetone. 2 g of KI and 20 ml of acetone were added to the chloride (0.5 g) and hexamethylenetetramine (1 g) in a flask with a ground-glass stopper. The mixture was shaken at 20° for a definite time and then titrated as indicated above. The following equation was used for finding the quantity of chloride, expressed as percent, entering into reaction:

$$\frac{hexa. \cdot \Theta - v}{chl.} \cdot \frac{c \cdot M}{10} \qquad (3)$$

where hexa. is the weight of hexamethylenetetramine; chl. is the weight of chloride; Θ is the amount of HCl in ml consumed in titration of 1 g of hexamethylenetetramine (found by titration of hexamethylene under the conditions indicated above); v is the volume of HCl in ml consumed in titration of the excess of hexamethylenetetramine; c is the concentration of acid (g-equiv./liter); M is the molecular weight of the chloride in question.

Results of the experiments are plotted in Figs. 1 and 2.

SUMMARY

1. It was found that hexamethylentetramine, in presence of formaldehyde, reacts with inorganic acids as a monoacidic base.

2. It was found that primary iodides of the allylic type quantitatively react with hexamethylenetetramine in equimolar ratios, and they can be determined by titration of the excess of hexamethylenetetramine with inorganic acids in presence of formaldehyde.

3. A study was made of the kinetics of reaction of KI with 1-chloro-3-methylbutene-2, 2-chloro-2-methylbutene-3 and their mixture, also of the reaction of KI with geranyl chloride in admixture with its tertiary isomers; it was found that only primary chlorides of the allylic type enter into reaction with KI, and that they can be quantitatively determined in presence of their tertiary isomers.

4. A chemical method was developed for quantitative determination of primary halogenated derivatives of the allylic type in presence of their tertiary isomers.

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THE VINYLATION OF MONOACETONE-D-GLUCOSE

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Several successful investigations on the vinylation of alcohols and phenols of various structures by the method of A. E. Favorsky and M. F. Shostakovsky [1] have recently been carried out. They include the preparation of vinyl derivatives of α-methylglucoside [2] and cellulose [3]. An unsuccessful attempt was made to vinylate monoacetone-D-glucose [4].

In the present work we studied the vinylation of isopropylidene-D-glucose. Direct vinylation of D-glucose was not promising (poor yield of vinyl ethers). Acetone derivatives were selected because of their higher thermal stability and ease of solution (in comparison with D-glucose) in organic solvents.

Monoacetone-D-glucose was prepared from diacetone-D-glucose by partial hydrolysis [5, 6]. Isopropylidene--D-glucose in a dioxan medium was treated with acetylene at 145-150° for 6-7 hours in presence of 20% of KOH (on weight of acetone derivative) under a pressure of 18-24 atm. The yield of trivinyl monoacetone-D-glucose was up to 44%.

EXPERIMENTAL

25 g of D-glucose and 500 ml of acetone were stirred for 2 hours at 25° in presence of concentrated sulfuric acid; after neutralization with ammonia, the filtrate was evaporated in vacuo to give 23-24 g (57-60%) of diacetone-D-glucose with m.p. 107-108°.

40 g of 1,2,5,6-diisopropylidene-D-glucose, 70 ml of 96% ethyl alcohol and 10 ml of conc. sulfuric acid were charged into a flask (fitted with a stirrer) at 20°. The solution of the resultant monoacetoneglucose was neutralized with ammonia and the filtrate was evaporated in vacuo on a water bath (50°). The residue was washed with ether. The yield of monoacetone-D-glucose was 26 g (76%), m.p. 159-160° [7]. This yield is higher than that obtained by the procedure previously described [5, 7].

Preparation of 2,5,6-trivinyl-1,2-isopropylidene-D-glucose. 25 g of 1,2-isopropylidene-D-glucose, 250 ml of dioxan and 5 g of KOH were charged into an autoclave. The acetylene pressure at 18° was 24 atm. Duration of vinylation 7 hours. Maximum pressure about 80 atm. The reaction mixture was filtered and then fractionally distilled. A pale-yellow, oily liquid separated which decolorized bromine water. The compound is readily soluble in organic solvents. Yield 15 g (44%).

B. p. 128-130° (1.5 mm), d_{20}^{20} 1.140, n_{20}^{20} 1.484, MR 76.20; calc. 75.10.

Found %: C 60.50, 60.12; H 7.21, 7.17. M 293.8. $C_{15}H_{22}O_6$. Calculated %: C 60.43, H 7.37. M 298.2.

The presence of three vinyl groups was established by hydrolytic oximation.

Hydrogenation of 3,5,6-trivinyl-1,2-isopropylidene-D-glucose. The following were placed in three flasks: 1) 1.17 g of the substance, 50 ml of ethyl alcohol, 1.5 g of Raney nickel; 2) 0.75 g of substance, 50 ml of ethyl alcohol, 1.5 g of Raney nickel; 3) (control) 50 ml of ethyl alcohcl, 1.5 g of Raney nickel. The flasks were shaken at room temperature for about 20 hours until hydrogen ceased to be absorbed.

Hydrogen consumptions were: 1) 262.4 ml H_2; 2) 159.9 ml H_2; 3) none. Calculated for three vinyl groups: 1) 267.2 ml of H_2; 2) 164.6 ml of H_2.

20 g of the substance was then hydrogenated for 40 hours, and about 4500 ml of hydrogen was absorbed. The

catalyst (Raney nickel, 3 g) was filtered off and the alcohol (100 ml) was distilled off. The main product – 3,5,6-triethyl-1,2-isopropylidene-D-glucose – was an oily, transparent liquid which did not decolorize bromine water. Yield 15 g (75%).

B. p. 114-115° (1.5 mm), d_{20}^{20} 1.099, n_D^{20} 1.454, MR 74.81; calc. 75.87.

Found %: C 58.92, 58.81; H 9.02, 9.07. M 300.2. $C_{15}H_{28}O_6$. Calculated %: C 59.23; H 9.21. M 304.2.

Partial hydrolysis of 3,5,6-trivinyl-1,2-isopropylidene-D-glucose gave 1,2-isopropylidene-D-glucose.

Complete hydrolysis both of trivinylmonoacetone-D-glucose and of the corresponding ethyl derivative gave D-glucose.

SUMMARY

1. 3,5,6-Trivinyl-1,2-isopropylidene-D-glucose was synthesized from 1,2-isopropylidene-D-glucose and acetylene.

2. Hydrogenation of trivinylmonoacetone-D-glucose gave 3,5,6-triethyl-1,2-isopropylidene-D-glucose.

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SYNTHESIS OF 2-VINYLPYRIDINE AND 2-VINYLQUINOLINE

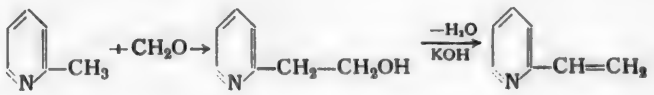
M. M. Koton and O. K. Surnina

Although 2-vinylpyridine has been known for a very long time [1], there has not hitherto been a satisfactory method of synthesis [2] enabling the monomer to be obtained in good yields and with a high degree of purity. A yield of 80% has, however, been claimed in a patent [3]. 2-Vinylquinoline has likewise been known for a long time [4], but a method of synthesis giving satisfactory yields has only recently been described, although the wide boiling range of the preparation indicates inadequate purity [5].

We required monomers with a high degree of purity for a study of the polymerization of 2-vinylpyridine and 2-vinylquinoline. For this purpose we had to modify the existing methods of synthesis.

EXPERIMENTAL

Synthesis of 2-vinylpyridine. 2-Vinylpyridine was obtained from α-picoline and paraformaldehyde by the following reaction:

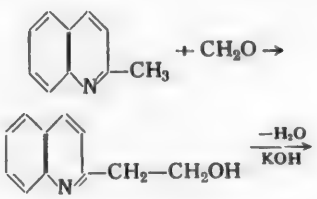


Into a 0.5-liter steel autoclave were charged 100 ml of freshly distilled α-picoline and 15 g of paraformaldehyde; an initial hydrogen pressure of 62 atm was established at room temperature. The autoclave was then heated for 7 hours at 140°. Unreacted α-picoline was distilled off from the reaction mixture, and the residual carbinol was twice distilled in vacuo. After purification by distillation, the 2-β-hydroxyethylpyridine had b.p. 102-103° (5 mm), n_D^{20} 1.5375 [6]. Yield 43%.

7.5 g of potassium hydroxide and a trace of phenyl-β-naphthylamine (polymerization inhibitor) were added to 17 g of 2-β-hydroxyethylpyridine in a distillation flask; distillation was started in a vacuum of 100 mm, which was later increased to 20 mm. The distilled 2-vinylpyridine was dried over potassium hydroxide and redistilled. Yield 81%. Constants are given in the table.

2-Vinylpyridine readily polymerizes in presence of initiators, starting from a temperature of 50°. The polymer obtained in presence of benzoyl peroxide is red in color. Block-polymerized 2-vinylpyridine (prepared in presence of 0.2% of azodiisobutyronitrile) is a colorless, transparent solid with a Vicat softening point of 83° (reprecipitated specimen); its characteristic viscosity η is 0.5; it readily copolymerizes with styrene, acrylonitrile and dienes.

Synthesis of 2-vinylquinoline. 2-Vinylquinoline was obtained from quinaldine and paraformaldehyde by the following sequence of reactions:



Physicochemical Properties of Monomers

Substance	Boiling point		n_D^{20}		d_4^{20}		MR_D		Content (in %)					
	found	literature data [12]	found	lit. data [13]	found	lit. data [14]	found	lit. data [14]	C		H		N	
									found	calculated	found	calculated	found	calculated
2-Vinylpyridine	64°5 (20 мм)	60° (17 мм)	1.5497	1.5495	0.9757	0.9770	31.33	34.40	80.02	80.00	6.85	6.66	13.16	13.33
2-Vinylquinoline.	104° (3 мм)	120—125 (17 мм)	1.6485	1.6439	1.0705	1.0692	52.79	—	85.50	85.15	6.00	5.80	9.19	9.03

Many authors [7] have described the synthesis of quinaldine. We tested various methods of synthesis [8, 9] and obtained the best results with the method of B. A. Porai-Koshits and coworkers [10] modified by using vinyl ethyl ether in place of vinyl butyl ether. The quinaldine obtained by this route had b.p. 118-120° (10 mm), n_D^{20} 1.6120. The picrate had m.p. 191.5-192° [7].

2-β-Hydroxyethylquinoline was preapred by a modification of the method of Bachman and Micussi [5]. 100 g of quinaldine, 90 g of 40% formaldehyde, 50 ml of alcohol and 50 ml of water were placed in a round-bottomed flask fitted with a reflux condenser, stirrer and thermometer. The flask was heated for 30 hours on a steam bath. The solvent was then distilled off in vacuo. The residual carbinol was purified by numerous recrystallizations from ether. The purified 2-β-hydroxyethylquinoline had m.p. 101-102° [4, 11].

Found %: N 8.40. $C_{10}H_{11}ON$. Calculated %: N 8.09.

Dehydration of 2-β-hydroxyethylquinoline was effected in similar fashion to the dehydration of 2-β-hydroxyethylpyridine. 2-Vinylquinoline was obtained in a yield of 57%. The constants of the monomer appear in the table.

Vinylquinoline polymerizes when heated in presence of initiators and forms colored, transparent solids with a Vicat softening point of 86° (reprecipitated specimen) and a characteristic viscosity [η] of 0.1. It readily copolymerizes with styrene, acrylonitrile and dienes.

Polymers of 2-vinylpyridine and 2-vinylquinoline, being polar compounds, are soluble in alcohols, chloroform and benzene; insoluble in hexane, ligroin and ethyl ether.

Attempts to prepared 2-vinyl-6-methylquinoline, 2-vinyl-8-methoxyquinoline and 2-vinyl-6-nitroquinoline were unsuccessful due to the substituted quinaldines not entering into condensation reaction with formaldehyde. Severe resinification resulted from attempts to obtain the corresponding aldehydes by treatment of the substituted quinaldines with selenium dioxide.

SUMMARY

An improved method of synthesis of 2-vinylpyridine and 2-vinylquinoline is proposed. This permits these substances to be obtained as monomers in good yields and with a high degree of purity.

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INVESTIGATION OF THE FORMATION OF DIACETYLENIC COMPOUNDS FROM MONOSUBSTITUTED ACETYLENE DERIVATIVES

I. THE MECHANISM OF FORMATION OF DIACETYLENIC COMPOUNDS

A. L. Klebansky, I. V. Grachev* and O. M. Kuznetsova

Compounds of the diacetylenic series were first prepared by oxidation of copper [1, 2], sodium [3] and magnesium bromide [4] derivatives of monosubstituted acetylenes by various oxidants. Yu. S. Zalkind [5] proposed a new method involving the action of a solution of cuprous chloride and ammonium chloride on monosubstituted acetylenes in presence of atmospheric oxygen. Only a few theories of the mechanism of this reaction have been put forward in the literature; the most interesting of these is the theory of Zalkind and coworkers [6] to the effect that the process starts with breakdown of the acetylenic compound into radicals which later join up to give a diacetylenic compound. The hydrogen formed during the reaction is either used up in hydrogenation of part of the original substance or is oxidized by oxygen of the air to water. This theory is insufficiently complete and not fully supported by facts. On the assumption of radical breakdown, the role of copper salts and atmospheric oxygen is obscure. It is also difficult to conceive of homolytic rupture of the C–H bond in the acetylenic derivative taking place in an aqueous medium at room temperature, for this process requires about 121 kcal/mole.

There is likewise inadequate evidence for the over-all mechanism of the process advanced by G. Mkryan and N. Papazyan [7]. The latter regard the process of transformation of methylacetylene into dimethyldiacetylene in presence of cuprous chloride and atmospheric oxygen as a sequence of alternating oxidations and reductions. Formation of diacetylenic compound is considered to be the result of interaction of the monosubstituted acetylenic derivative with partly oxidized catalyst. This theory is of definite interest, but not all of the steps have been experimentally proven.

In the present work an attempt was made at further study of the formation of diacetylenic compounds from monosubstituted derivatives of acetylene in presence of copper salts. We concentrated on investigation of the reaction of conversion of dimethylethynyl carbinol into 2,7-dimethyloctadiene-3,5-diol-2,7. We also studied the formation of other diacetylenic compounds with the aim of clarifying the influence of the structure of the acetylenic compounds on the process, and also of elucidating the mechanism of the reaction. We are certain that the ability of monosubstituted derivatives of acetylene to form diacetylenic compounds must be closely bound up with their structural features and in particular with the presence of the easily polarizable triple bond and a labile acetylenic hydrogen. The basis of formation of the diacetylenic compounds is oxidation of the monosubstituted derivatives by salts of bivalent copper. This reaction must be preceded, however, by ionization of the acetylenic compound, and this is facilitated by the presence of hydroxyl ions in the aqueous solution of copper salts.

We consider the oxidation of the acetylide ion to a diacetylenic compound to proceed in two steps. At first there is oxidation of acetylide ions to radicals which then with great rapidity recombine to form a molecule of diacetylenic compound. Consequently, the process of formation of the diacetylenic compound may be represented by the following scheme:

$$RC{\equiv}CH \rightleftarrows R{-}C{\equiv}\bar{C}: + \overset{+}{H} \qquad (1)$$

$$R{-}C{\equiv}\bar{C}: + \overset{++}{Cu} \rightarrow RC{\equiv}C^{\cdot} + Cu^{+} \qquad (2)$$

$$R{-}C{\equiv}C^{\cdot} + {}^{\cdot}C{\equiv}C{-}R \rightarrow R{-}C{\equiv}C{-}C{\equiv}C{-}R \qquad (3)$$

* Deceased.

The rate of the first step of the process can vary in dependence on the reaction conditions; the mechanism can likewise vary with the conditions. In an acid medium, which is present when acetylenic compounds are oxidized in presence of cuprous chloride and atmospheric oxygen, the acetylide ion can be formed at the expense of secondary dissociation of the complex ion $[RC \equiv C(CuCl \cdot NH_4Cl)]^-$ which is formed. If the reaction is carried out with the help of a bivalent copper salt in an alkaline (ammoniacal) solution, the acetylene derivative is ionized at the expense of formation of unstable substituted copper acetylides. In both cases the formation of acetylide ion is clearly the rate-determining step for the over-all reaction. The acetylide ions formed are subsequently extremely quickly oxidized to radicals which combine to form a diacetylenic compound. There is little probability of the accumulation in the solution, during the reaction, of appreciable quantities of acetylide ions, and in turn of free radicals, in view of their instability.

The data obtained in the work, together with the literature data, permit the conclusion that the transformation of monosubstituted acetylenic derivatives into diacetylenes in presence of cuprous chloride in ammonium chloride solution is accompanied by oxidation of univalent copper to bivalent (at the expense of oxygen of the air), which then enters into reaction with the acetylenic compound, oxidizing it to a diacetylenic compound. Under these conditions we thus have the following reactions:

$$2Cu^+ + {}^1/_2O_2 + H_2O \rightarrow 2Cu^{++} + 2OH^- \quad (4)$$

$$2Cu^{++} + 2R{-}C{\equiv}CH \rightarrow 2Cu^+ + R{-}C{\equiv}C{-}C{\equiv}C{-}R + 2H^+ \quad (5)$$

It is therefore understandable that in absence of atmospheric oxygen diacetylenic compounds cannot be formed when using salts of univalent copper. It follows from these considerations that the employment of salts of univalent copper together with oxygen of the air is not generally essential for this reaction, as we confirmed by realizing the reaction of monosubstituted derivatives of acetylene with salts of bivalent copper under appropriate conditions. This work established that salts of bivalent copper enter into reaction with acetylenic derivatives only if the solution receives an addition of caustic alkali (NaOH, ammonia, pyridine, triethylamine). This requirement is evidently associated with the necessity for neutralization of the hydrogen ions released during reaction (5). When using salts of univalent copper, however, this addition is unnecessary because the hydroxyl ions needed for neutralization are present due to oxidation of univalent copper to divalent.

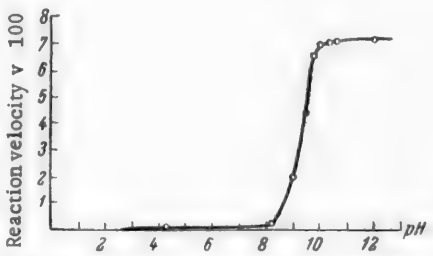

Fig. 1. Reaction velocity as a function of pH.
Reaction velocity is expressed as the number of moles/liter of dimethylethynyl carbinol reacted after 60 minutes.

It was further established that oxidation of dimethylethynyl carbinol with cupric chloride proceeds relatively rapidly on addition of ammonia, and very much more slowly on addition of sodium hydroxide, since when using ammonia (not fewer than 4 moles per mole of cupric chloride) a homogeneous solution of complex salts of bivalent copper is formed. Examination of the products of reaction and their quantitative determination enables us to conclude that equation (5) applies to the oxidation of dimethylethynyl carbinol with cupric chloride in ammonia solution. It follows from the experimental data that the process of formation of 2,7-dimethyloctadiene-3,5-diol-2,7 from dimethylethynyl carbinol involves oxidation of the latter by bivalent copper and is accompanied by rise in acidity of the solution.

A study of the kinetics of oxidation of dimethylethynyl carbinol with cupric chloride in ammoniacal solution established that the reaction rate depends both on the concentration of the original acetylenic alcohol and on the concentration of cupric chloride. The oxidation of dimethylethynyl carbinol by cupric chloride is a second order reaction. The velocity constants of the reaction, calculated from the equation for a bimolecular reaction, remained constant within the limits of error, as shown in Table 1.

The hydrogen ion concentration markedly influences the rate of the reaction in question. As we see from Fig. 1, the reaction acquires appreciable speed at pH > 7, which may be attributed to the increase in ionization of the acetylenic compound and is consistent with the proposed reaction mechanism (see scheme).

TABLE 1

a) Dependence of velocity constant of the reaction on the concentration of dimethylethynyl carbinol with a 1 : 1 molar ratio of $CuCl_2$ to d.e.c.

Starting concentration of dimethylethynyl carbinol (moles/liter)	0.05	0.1	0.15	0.25	0.35
K · 100	4.908	4.697	4.801	4.921	4.882

b) Dependence of the velocity constant of the reaction on the degree of conversion of dimethylethynyl carbinol with a 1 : 1 molar ratio of $CuCl_2$ to d.e.c.

Degree of conversion (in % of reacted dimethylethynyl carbinol)	6.47	17.05	29.75	45.67
K · 100	4.852	4.803	4.911	4.902

It should be noted that the reaction rate only increases to a certain limit evidently due to attainment of the maximum degree of dissociation of the ammonium base (since the pH value changes with the ammonia concentration). This is consistent with the influence of ammonium salts on the reaction rate. Table 2 indicates that addition of ammonium salts appreciably slows down the reaction since ammonium salts suppress to some extent the dissociation of the ammonia base.

TABLE 2

Influence of Ammonium Salts on the Oxidation of Dimethylethynyl Carbinol

Molar ratio of $CuCl_2$ to d.e.c. = 1

Moles of ammonium salts per mole of dimethylethynyl carbinol			pH	% of dimethylethynyl carbinol reacted after 60 min.
NH_4Cl	NH_4CNS	NH_4NO_3		
—	—	—	9.5	30.07
0.5	—	—	9.4	20.17
1.0	—	—	9.3	13.85
2.0	—	—	9.3	14.05
—	2.0	—	9.3	15.13
—	—	2.0	9.4	16.25

Addition of salts of univalent copper during oxidation of dimethylethynyl carbinol with cupric chloride in ammonia solution has no effect on the reaction rate, which indicates that the ions of univalent copper formed during the reaction have no appreciable influence on the process.

Comparative oxidation data for treatment in aqueous pyridine solutions with cupric and cuprous chlorides in presence of oxygen are given in Table 3 for the following compounds that we synthesized: phenylacetylene, butylacetylene, methylethynyl carbinol, diphenylethynyl carbinol, phenylethynyl carbinol, butyn-1-ol-4, dimethylethynyl carbinol.

These compounds can be arranged in the following order in respect of their ability to form diacetylenic compounds:

$$C_6H_5C{\equiv}CH > C_6H_5CHOHC{\equiv}CH > CH_3CHOHC{\equiv}CH >$$
$$> (C_6H_5)_2COHC{\equiv}CH > (CH_3)_2COHC{\equiv}CH >$$
$$> OHCH_2CH_2C{\equiv}CH > CH_3CH_2CH_2CH_2C{\equiv}CH.$$

TABLE 3

Degree of Conversion of Monosubstituted Acetylenes after 60 Minutes (in % of Reacted Compound)

Acetylenic compound	Oxidant	
	$CuCl+O_2$	$CuCl_2$
$C_6H_5C{\equiv}CH$	82.55	25.14
$C_6H_5CHOHC{\equiv}CH$	72.35	21.50
$CH_3CHOHC{\equiv}CH$	60.7	15.25
$(C_6H_5)_2COH{-}C{\equiv}CH$	47.13	14.33
$(CH_3)_2C(OH)C{\equiv}CH$	30.13	30.55
$OHCH_2CH_2C{\equiv}CH$	22.14	5.41
$CH_3CH_2CH_2CH_2C{\equiv}CH$	17.11	2.0

Table 4 shows that a similar order applies to carboxylic acids with identical substituents in respect of their ionizing ability; this is associated with the identical influence of substituents on the mobility of the hydrogen atom both in an acetylenic derivative and in the corresponding carboxylic acid.

TABLE 4

Ionization Constants of Carboxylic Acids

Carboxylic acid	Ionization constant at 25°	pK ($-\log K$)
$(C_6H_5)_2C(OH)COOH$	$9.2 \cdot 10^{-4}$	3.05
C_6H_5COOH	$5.86 \cdot 10^{-4}$	3.23
$C_6H_5CHOHCOOH$	$4.2 \cdot 10^{-4}$	3.38
$CH_3CHOHCOOH$	$1.36 \cdot 10^{-4}$	3.87
$(CH_3)_2C(OH)COOH$	$1.03 \cdot 10^{-4}$	3.99
$OHCH_2CH_2COOH$	$2.95 \cdot 10^{-5}$	4.53
$CH_3CH_2CH_2CH_2COOH$	$1.56 \cdot 10^{-5}$	4.82

Benzilic acid constitutes an exception, its position in the acid series not coinciding with that of diphenylethynyl carbinol in the series of acetylenic compounds. The relation between degree of ionization of the above acids and the susceptibility to oxidation of the corresponding acetylenic derivatives to diacetylenic compounds is plotted in Fig. 2. This diagram shows the existence of a roughly linear dependence of the rate of oxidation of acetylenic compounds on the logarithm of the ionization constants of the corresponding carboxylic acids. This relationship applies both for oxidation with cupric chloride and for oxidation with cuprous chloride and oxygen. Consequently, the rate of formation of diacetylenic compounds is a linear function of the mobility of the acetylenic hydrogen. This confirms the hypothesis that the rate of the over-all reaction is governed by its first step.

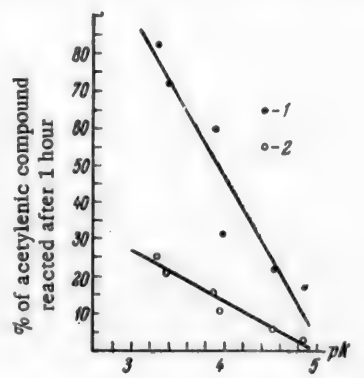

Fig. 2. Relation between rate of oxidation of monosubstituted acetylenic derivatives of acetylene and pH of the carboxylic acids.
1) CuCl, 2) $CuCl_2$.

A polarographic investigation of the system dimethylethynyl carbinol – $CuCl_2$ in ammonia solution showed the absence of appreciable amounts of any copper derivatives of dimethylethynyl carbinol from the reaction mixture. This confirms the earlier conclusion that the rate of the second step of the process is higher than that of the first step. Evidently the acetylide ion formed during the reaction is immediately oxidized and does not accumulate

in the solution. Under other conditions, for example on oxidation in the air of monosubstituted acetylenic derivatives in a solution of cuprous chloride and ammonium chloride, the formation of stable intermediate compounds of acetylenic derivative with copper salts is entirely possible. It was also established that the pH falls sharply when n-butylacetylene, phenylacetylene, methylethynyl carbinol, phenylethynyl carbinol and dimethylethynyl carbinol are dissolved in a solution of cuprous chloride and ammonium chloride; this is associated with the formation of a complex compound of acetylenic derivative with $CuCl - NH_4Cl$, in analogy with the behavior of acetylene and vinylacetylene [8].

The fall in pH of a $CuCl - NH_4Cl$ solution on interaction with dimethylethynyl carbinol is shown in Fig. 3. This fall can only be attributed to ionization of the acetylenic hydrogen.

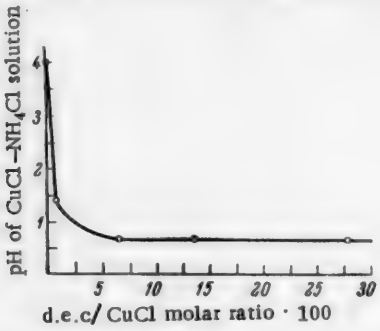

Fig. 3. Change of pH of $CuCl - NH_4Cl$ solution in dependence on the d.e.c/ CuCl molar ratio.

Experiments established that solutions of complex compounds of dimethylethynyl carbinol with $CuCl-NH_4Cl$ are oxidized to the diacetylenic glycol 2,7-dimethyl--3,5-diol-2,7. It should be pointed out that replacement of salts of bivalent copper in this reaction by other oxidants (ferric chloride, sodium hypochlorite, potassium ferricyanide, etc.) did not lead to formation of a diacetylenic compound from dimethylethynyl carbinol. On carrying out electrolytic oxidation of dimethylethynyl carbinol, we only obtained the diacetylenic glycol when using a copper anode and copper ions were present in the electrolyte. Evidently the degree of ionization of acetylenic derivatives in aqueous (and even in caustic alkaline) solutions but in the absence of copper salts is so insignificant, and the content of acetylide ions in the solutions is so small, that appreciable amounts of diacetylenic compound cannot be formed when using other oxidants.

In our opinion, the role of bivalent copper during the second reaction step consists in interaction with the acetylide ion formed, with the result that the latter is converted into a substituted ethynyl radical while the bivalent copper is reduced to univalent. It must be noted that the ability of copper ions to accept, or donate, an electron from, or to, organic or inorganic ions with formation of free radicals has been mentioned in the literature [9-11]. There are no direct indications, however, of the ability of monosubstituted acetylenes to give free radicals of substituted acetylide under conditions similar to those of the reaction here studied. The fundamental possibility of formation of these radicals follows from the work of A. E. Favorsky, who obtained a diacetylenic compound on heating copper tert.-butylacetylide [12]. We also demonstrated this possibility in the case of reaction of copper phenylacetylide with isopropylbenzene when the formation of phenylacetylene was qualitatively shown. An alternative mechanism for formation of the latter involves the assumption of formation of the free phenylethynyl radical as an intermediate:

$$C_6H_5C{\equiv}CCu \rightarrow C_6H_5C{\equiv}C^{\cdot} + Cu^{\cdot}$$

$$C_6H_5C{\equiv}C^{\cdot} + HCC_6H_5(CH_3)_2 \rightarrow C_6H_5C{\equiv}CH + {}^{\cdot}CC_6H_5(CH_3)_2$$

It is difficult to obtain direct proof of the formation of free radicals on oxidation of monosubstituted acetylene derivatives with copper salts in aqueous solutions due to their great reactivity and their extremely short life. Indirect evidence is afforded by the formation of mixed diacetylenic compounds in Baeyer's experiments [2] when a mixture of two substituted copper acetylides was subjected to oxidation, also by the experiments of Nogaideli and Shvangiradze [13] who oxidized a mixture of two acetylenic alcohols. Formation in these cases of mixed diacetylenic compounds (as the main products of reaction) is best explained on the assumption of formation of free radicals which then recombine.

The third and last step in formation of diacetylenic compounds (recombination of the free radicals to a diacetylene) has not been the subject of special study, and in our opinion it does not call for special proof in view of the well-known susceptibility of free radicals to recombination. Formation of the end product of oxidation of dimethylethynyl carbinol does nevertheless afford quantitative evidence that the free radicals exclusively enter into a recombination reaction.

The data obtained in this work enable us to propose a method of preparation of diacetylenic compounds consisting in the reaction of aecetylenic derivatives with aqueous solutions of salts of bivalent copper in presence of bases.

SUMMARY

1. A mechanism of the formation of diacetylenic compounds from monosubstituted acetylenic derivatives on reaction with copper salts is advanced.

2. It is shown that formation of diacetylenic compounds in aqueous solutions proceeds by an ionic-radical mechanism. The first step is formation of acetylide ions facilitated by copper ions. The acetylide ions are then oxidized by ions of bivalent copper to radicals which recombine to give a molecule of diacetylenic compound.

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SYNTHESIS OF ORGANOSILICON COMPOUNDS

IV. HYDROLYSIS OF DIMETHYLDICHLOROSILANE BY METHYL ALCOHOL WITH FORMATION OF LINEAR POLYSILOXANES AND METHYL CHLORIDE

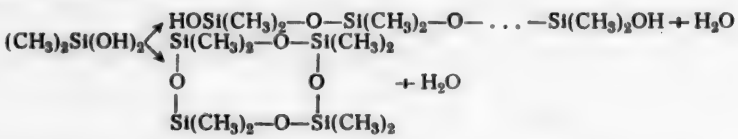
V. S. Fikhtengolts, A. L. Klebansky and K. A. Rzhendzinskaya

Dimethyldichlorosilane is converted into high-molecular compounds by hydrolysis which proceeds according to the equation

$$(CH_3)_2SiCl_2 + 2H_2O \rightarrow (CH_3)_2Si(OH)_2 + 2HCl.$$

The resultant dimethylsilanediol spontaneously anhydridizes with the result that Si—O—Si bonds are developed. Subsequent polycondensation of the products of hydrolysis to rubberlike material is effected by heating with a suitable catalyst like H_2SO_4, $FeCl_3$, etc. [1].

Hydrolysis of dimethyldichlorosilane with excess of water gives compounds of two types — linear and cyclic — in approximately equal quantities [2].



Cyclic polysiloxanes consist mainly of tetramer. Low-molecular cyclic polysiloxanes (3-10 silicon atoms) can be distilled to leave a residue of linear and higher cyclic polysiloxanes. Formation of low-molecular cyclic forms is promoted by an acid medium during hydrolysis and by the presence of water-miscible solvents. An alkaline medium favors an increased content of high-molecular linear polysiloxanes. Predominantly linear polysiloxanes are obtained when dimethyldialkoxy derivatives are hydrolyzed by gradual addition of water introduced in quantity less than that theoretically calculated [3]. In this case hydrolysis is accompanied by anhydridization of the silanediol formed.

Dialkoxy derivatives are obtained by the action of alcohols on dimethyldichlrosilane:

$$(CH_3)_2SiCl_2 + 2ROH \rightarrow (CH_3)_2Si(OR)_2 + 2HCl.$$

The yield of dialkoxysilanols, however, is relatively low. For example, we find about 65% for dimethyldiethoxysilane. The remainder is transformed into high-molecular products. When the synthesis is carried out in presence of alumina, which binds the hydrogen chloride, the yield is increased to 80% and the quantity of high-molecular residue is lower. A similar rise in yield of ethoxy derivatives is observed when operating in presence of quinoline or dimethylaniline [4]. It may be assumed that the high-molecular residue originates from hydrolysis of the diethoxy derivatives by water released during interaction of hydrogen chloride with the alcohol. This led us to consider the possibility of gradual hydrolysis of dimethyldichlorosilane with formation of linear polysiloxanes by reacting an alcohol with hydrogen chloride. When using methyl alcohol we could expect the formation of methyl chloride and regeneration in this manner of the original substance consumed during synthesis of dimethyldichlorosilane.

Experiments on the hydrolysis of dimethyldichlorosilane by methyl alcohol were conducted in the following manner. Dimethyldichlorosilane was run into methyl alcohol while cooling and stirring. At this stage dimethyldimethoxysilane was formed and the hydrogen chloride dissolved in the reaction mixture:

$$(CH_3)_2SiCl_2 + 2CH_3OH = (CH_3)_2Si(OCH_3)_2 + 2HCl \quad (1)$$

The stirrer reaction mixture was then heated on a water bath. This causes gradual hydrolysis of the dimethyldimethoxysilane, and the methyl chloride distils off:

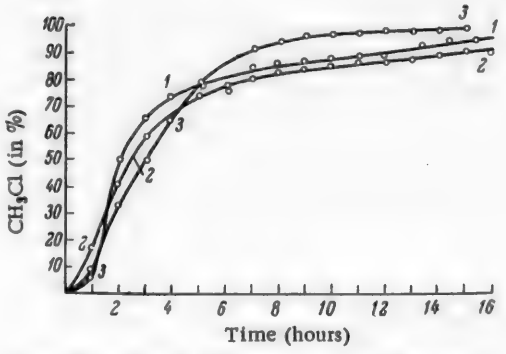
$$CH_3OH + HCl \rightarrow CH_3Cl + H_2O \quad (2)$$

$$(CH_3)_2Si(OCH_3)_2 + H_2O \rightarrow CH_3OSi(CH_3)_2OH + CH_3OH \quad (3)$$

$$CH_3OSi(CH_3)_2OH + HOSi(CH_3)_2OCH_3 \rightarrow CH_3OSi(CH_3)_2{-}O{-}Si(CH_3)_2OCH_3 + H_2O \rightarrow$$
$$\rightarrow CH_3OSi(CH_3)_2{-}O{-}Si(CH_3)_2OH + CH_3OH \text{ etc.} \quad (4)$$

The layer of products of hydrolysis was separated, washed with water and dried with calcined sodium sulfate.

It was established that the excess of methanol must be such as to ensure complete solution of the hydrogen chloride released during the first stage of the reaction in order to ensure completeness of formation of methyl chloride in the second stage. The required quantity of alcohol was found to be 250% of the theoretical. It was also found that anhydrous methanol (d^{20} 0.790) was not essential, and its replacement by rectified material (d^{20} 0.795) did not appreciably affect the results of hydrolysis. It was also established that addition of the dimethyldichlorosilane to the methanol in the course of 15-30 min followed by stirring for 45-60 min ensures a yield of 97-99% of methyl chloride. The yield of CH_3Cl fell to 90% if the dimethyldichlorosilane was added in 1-2 min.



Rate of liberation of methyl chloride during hydrolysis.
1) Rapid heating of bath; 2) bath previously heated to 50° and rapidly heated; 3) gradual heating of bath.

The temperature of the reaction mixture during the first stage of the process is bound to have a marked influence on the yield of methyl chloride because with falling temperature the solubility of hydrogen chloride increases. At first the experiments were therefore performed at a reaction mixture temperature of 5-10°. It was subsequently established, however, that a 250-300% excess of methanol ensures complete solution of HCl even at 15-20° and the yield of methyl chloride is not reduced.

The purity of the methanol is a more important factor. First grade synthetic methanol resulted in nearly theoretical yields of methyl chloride. This grade of methanol is not contaminated with ethers and carbonyl compounds. The use of wood spirit (containing the above-mentioned impurities) caused the yield of CH_3Cl to drop to 73%. After this methanol had been purified by boiling with alkaline permanganate, the yield of CH_3Cl rose to 95%. Addition of 5% of acetone to the purified alcohol again caused the yield of CH_3Cl to drop (to 71%). In the light of this experience, it is necessary to employ first grade synthetic methanol, with a minimum content of impurities, for hydrolysis of dimethyldichlorosilane.

The second stage – hydrolysis of dimethyldimethoxysilane and simultaneous release of methyl chloride on heating – requires 15-17 hours for its completion. We were unable to speed up this process by adding 3-5% of $FeCl_3$ or $ZnCl_2$ activated with hydrogen chloride by formation of complexes. Introduction of sulfuric acid, which promotes growth of polysiloxane molecules, likewise did not accelerate the process. Rapid heating on the water bath also failed to shorten the duration of the second stage. As we see from the diagram, the rate of release of CH_3Cl under these conditions only increases in the first hours of heating and then falls below the rate obtained with gradual heating of the bath. Moreover, rapid heating also increases the loss of CH_3Cl. In the course of the first 5 hours 70-80% of the total CH_3Cl is usually evolved; another 10-12 hours is needed for separation of the remaining 20-30%. It might appear to be expedient to ignore this 20-25% of CH_3Cl and shorten the duration of

the second stage appreciably. Special experiments showed, however, that shortening of the heating period led to fall in the yield of products of hydrolysis.

TABLE 1

Yield of Products of Hydrolysis in Dependence on Duration of Heating

Duration of heating (hr)	Yield (in %)		Average molecular wt. of polysiloxanes •	Methoxyl number (% of methoxy groups)	
	CH_3Cl	of polysiloxanes		calculated	found
2	50	25.6	1500	2.07	1.84
5	70	56.5	1400	2.22	1.90
8	74	77.1	1375	2.25	2.00
14	82	79.3	1200	2.58	1.70

• Determined by the cryoscopic method.

Since the principal desired products of hydrolysis of dimethyldichlorosilane are polysiloxanes, the attainment of maximum yield of the latter requires that the second stage of the process should be prolonged until liberation of methyl chloride has entirely ceased. The last two columns of Table 1 will be discussed below.

The investigations described above have thus established the following conditions for hydrolysis. To a synthetic first-grade methanol (rectified, d^{20} 0.795), taken in double the quantity of dimethyldichlorosilane (300% excess), the whole of the dimethyldichlorosilane is added in the course of 15-30 minutes with stirring and with a temperature of 15-20° in the reaction zone; stirring is then continued for 45-60 minutes. The reaction mixture is then gradually heated at the boil with stirring on a water bath under a reflux condenser. Heating is continued until the methyl chloride has been completely removed, the rate of removal being regulated by the bath temperature. The reaction mixture is later cooled, and the resultant two layers are separated. Unreacted methanol is distilled off from the upper, aqueous alcoholic, layer. The lower layer (containing the products of hydrolysis) is washed with hot water until neutral, and dried either by heating in vacuo to 120° or with calcined sodium sulfate. Data for some hydrolysis experiments are given in Table 2.

TABLE 2

Hydrolysis of Dimethyldichlorosilane with Methanol

Quantity of starting substances (in g)		Excess of CH_3OH (in %)	Duration (hours)		Yield of CH_3Cl		Yield of hydrolyzate		CH_3OH recovered	
$(CH_3)_2SiCl_2$	CH_3OH		of 1st stage	of 2nd stage	(in g)	(in %)	(in g)	(in %)	(in g)	% of excess of CH_3OH
250	434	250	1	16	194.5	99.4	142.0	99.0	273	88
300	600	300	1	17	227.2	96.7	169.1	98.3	434	96
357	748	320	2	15	278.0	99.5	204.0	99.5	549	96

Our view on the mechanism of this process of hydrolysis are given above. We considered it necessary to submit some experimental proofs of the proposed mechanism. With the objective of verifying the formation of dimethyldimethoxysilane in the first stage of hydrolysis, an attempt was made to isolate it after preliminary neutralization of the HCl (with zinc). The resultant $ZnCl_2$ dissolves in the methanol, and ultimately the dimethyldimethoxysilane forms a layer. The separated product had b.p. 81-83°, which is close to the literature value of 81-82° [5]. Yield about 65%.

In the second stage of the process the dimethyldimethoxysilane is hydrolyzed by water formed by interaction

of hydrogen chloride with methanol. Another possibility, however, is direct reaction of hydrogen chloride with methoxy groups, likewise accompanied by formation of hydroxyl groups and liberation of methyl chloride.

$$CH_3O—Si(CH_3)_2OCH_3 + HCl = CH_3O—Si(CH_3)_2OH + CH_3Cl$$

In order to decide which of these mechanisms was really involved, the following experiment was run. To methyl alcohol saturated with hydrogen chloride (HCl content 23.3%) was added, with stirring in the cold, a previously prepared quantity of dimethyldiethoxysilane. The mixture was refluxed while being stirred; the reflux condenser was attached to two traps; the first was cooled with ice and salt, and the second with solid carbon dioxide. Reaction of hydrogen chloride with alkoxy groups of dimethyldiethoxysilane would have been expected to yield ethyl chloride (b.p. 13°) and this would be condensed in the first trap. But if hydrolysis occurs with the help of water released by interaction of hydrogen chloride with methanol, then methyl chloride should separate (b.p. −24°), and the latter could only condense in the second trap. In the experiment condensation was observed only in the second trap.

Since the formation of methyl chloride proceeds slowly, the water thereby released is in deficiency in relation to the dimethyldimethoxysilane hydrolyzed by it. Moreover, water is separated uniformly throughout the whole of the volume of reaction mass, and this could not be achieved by dropwise addition in which case a local excess of water is created in the area received by the drop. Hydrolysis of alkoxysilanes with a deficiency of water proceeds with formation of linear polysiloxanes [3]. Consequently, the optimum conditions for formation of linear polysiloxanes are set up in the foregoing method of hydrolysis. In this case the methoxyl groups are hydrolyzed at one end of the chain, due to which the polysiloxane molecule cannot undergo cyclization (see equations 3 and 4). The data of the last two columns of Table 1 confirm this mechanism of hydrolysis. Molecular weight determinations were made on the products of hydrolysis at different stages of the process. The fall in average molecular weight in course of the process is explained by the increase content in the products of low-molecular polysiloxanes due to decrease in solubility of the latter in the reaction mass in which the content of dimethyldimethoxysilane is decreasing and that of water is increasing. The methoxyl number of each average molecular weight was calculated on the assumption that each segment contains one methoxyl and one hydroxyl group. As we see from Table 1, the methoxyl groups found in the initial stage of hydrolysis by the Zeisel method are close to the theoretical values, thus affording further evidence of the linearity of the polysiloxanes obtained. In course of hydrolysis the discrepancy increases since the proportion of completely hydrolyzed molecules of polysiloxanes increases; at the end of the hydrolysis, all of the polysiloxane molecules are completely hydrolyzed. The absence of low-molecular cyclic polysiloxanes is indicated by the absence of distillate when the hydrolyzate is dried in vacuo at 120° (under these conditions cyclic products up to hexamer inclusive would have distilled off).

TABLE 3

Physicomechanical Characteristics of Vulcanizates

Polycondensation catalyst	% of catalyst	Filler					
		SiO_2 (50% of wt. of rubber)			TiO_2 (150% of wt. of rubber)		
		tensile strength kg/cm²	relative elongation (in %)	coefficient of frostresistance at −55°, 100% elongation	tensile strength kg/cm²	relative elongation (in %)	coefficient of frostresistance at −55°, 100% elongation
H_2SO_4	2	37	263	0.5	27	213	0.8
$FeCl_3$ (anhydrous) .	1	36	217	0.5	27	235	0.7
HI	1.5	42	220	0.9	28	243	0.9
$HCl + ZnCl_2$ . . .	4	37	265	—	22	250	0.4

Linear polysiloxanes obtained by the above method of hydrolysis are capable of condensing to rubbery polymer

under the influence of the usual catalysts like H_2SO_4 and $FeCl_3$. We also established that a 40-50% solution of HI and a solution of $ZnCl_2$ in HCl ($ZnCl_2 \cdot 2HCl$) are polycondensation catalysts. Standard rubber mixes prepared from these rubbers gave fully satisfactory results after vulcanization (Table 3).

All the rubbers were 100% soluble in benzene (absence of cross-linking of chains).

The method described is suitable also for hydrolysis of other methylchlorosilanes for the purpose of preparing heat-resistant oils and resins. Nearly quantitative separation of methyl chloride is likewise secured in these cases (Table 4).

TABLE 4

Hydrolysis of Methylchlorosilanes with Methanol

Starting substance	Quantity (in g)	CH_3OH		Duration (in hours)		Yield in CH_3Cl	
		(in g)	excess (in %)	of 1st stage	of 2nd stage	(in g)	(in %)
CH_3SiCl_3	53.5	139.5	300	1	12	52	95.6
$(CH_3)_3SiCl$ . . .	204	234.5	250	1	14	103	97.3

Hydrolysis of methyltrichlorosilane gave a transparent gel which hardened in the air. Hydrolysis of trimethylchlorosilane gave a readily mobile oil (hexamethyldisiloxane). Hydrolysis by the same method of mixtures of methyltrichlorosilane and trimethylchlorosilane or dimethyldichlorosilane can lead to different resins whose properties will depend on the ratio and nature of the components. Hydrolysis of mixtures of dimethyldichlorosilane and trimethylchlorosilane with excess of methanol can give stable oils whose consistency will depend on the ratio of components. Thus, hydrolysis of a mixture of $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$ in the weight ratio of 4 : 1 gave an oil with an average molecular weight of 1150 (15 atoms of Si in the molecule). A total of 9% came over on distillation of the oil in vacuo at 210°. The stability of the oil was confirmed by its nonsusceptibility to polycondensation in presence of conc. H_2SO_4 even with heating. A considerable proportion of the methyl chloride consumed can thus be regenerated by utilizing the secondary products of synthesis of dimethyldichlorosilane.

SUMMARY

1. A method of production of linear polysiloxanes directly from dimethyldichlorosiloxane by hydrolysis with methanol was developed.

2. It was found that the use of 250-300% excess of methanol enables the methyl chloride consumed in the synthesis of the dimethyldichlorosilane to be nearly fully regenerated.

3. This method is shown to be applicable to the preparation of polysiloxane resins and stable oils by utilizing secondary products of synthesis of dimethyldichlorosilane, likewise with regeneration of the methyl chloride consumed in the synthesis of these methylchlorosilanes.

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SYNTHESIS OF SOME ALKYLBENZENES AND ALKYLCYCLOHEXANES OF THE COMPOSITION C_{14}–C_{15}

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Alkylbenzenes with a branched paraffinic chain obtained up to now were synthesized mainly by alkylation of benzene with tertiary alcohols or alkyl halides in presence of $AlCl_3$ [1]. High yields are obtained with low-molecular tertiary alcohols and alkyl halides, but yields are very much lower on passing to higher molecular alcohols. Whereas the alkylation of benzene with tert. butyl alcohol gave a 70% yield of alkylation product, alkylation with dimethylisobutyl carbinol and dimethyl-tert.-butyl carbinol gave yields of only 35% and 7% respectively. It is obvious, of course, that with increasing molecular weight of the tertiary alcohols the purity of the resultant hydrocarbons will also become problematical, due to the strong isomerizing action of aluminum chloride. An attempt to synthesize alkylbenzenes by condensation of bromobenzene with tertiary alkyl chlorides by the Würtz-Fitting reaction led only to diphenyl and olefinic hydrocarbons [2].

In view of the above considerations, interest was attached to a study of the possibilities of synthesis of alkylbenzenes by the Würtz-Grignard scheme. Buu-Hoi and Cagniant [3] condensed tert.-butyl chloride with the Grignard reagent from 1,3-dimethyl-4-bromobenzene and obtained a yield of 17%. We proceeded on similar lines in the present work and carried out 5 syntheses (Table 1) of previously unprepared alkylbenzenes, operating both in ether and (syntheses 3–5) in n-heptane.

TABLE 1

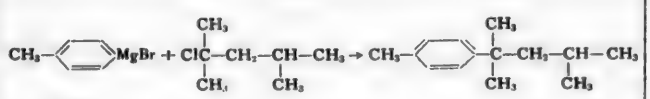
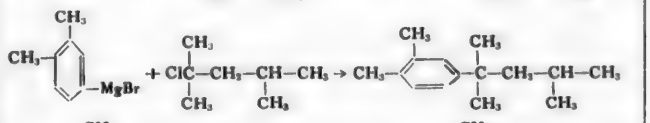
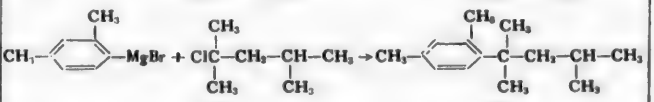
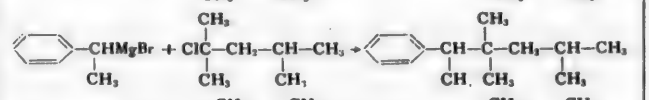
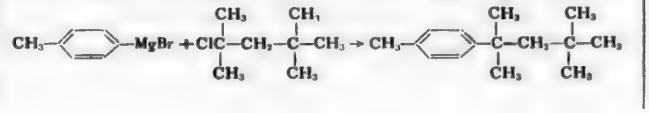
Synthesis No.	Reaction	Yield (in %) in ether	Yield (in %) in heptane
1		10	—
2		4	—
3		5	12
4		4	16
5		0	4

TABLE 2

Properties of Prepared Alkylbenzenes and Alkylcyclohexanes

Hydrocarbon	Boiling point (pressure in mm)	Setting point	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated*	Found (%) C	Found (%) H	Calculated (%) C	Calculated (%) H
1-Methyl-4-(1,1,3-trimethylbutyl)-benzene	75—77 (2)	—	1.5003	0.8813	63.55	63.58	88.43	11.66	88.35	11.65
1-Methyl-4-(1,1,3-trimethylbutyl)-cyclohexane	85 (4)	—95° (glass)	1.4550	0.8246	64.61	64.65	85.61	14.28	85.63	14.37
1,2-Dimethyl-4-(1,1,3-trimethylbutyl)--benzene	115—117 (13)	—	1.5013	0.8802	68.43	68.29	88.15	12.10	88.16	11.84
1,2-Dimethyl-4-(1,1,3-trimethylbutyl)--cyclohexane	115 (12)	—80 (glass)	1.4589	0.8321	69.12	69.27	85.60	14.25	85.63	14.37
1,3-Dimethyl-4-(1,1,3-trimethylbutyl)--benzene	131 (28) 107—108 (8) **	—	1.5021 1.5008	0.8837 0.8811	68.25 68.41	68.29	88.29, 88.31	11.76, 11.80	88.16	11.84
1,3-Dimethyl-4-(1,1,3-trimethylbutyl)--cyclohexane	107 (8)	—80 (glass)	1.4598	0.8340	69.08	69.27	85.70	14.38	85.63	14.37
2,4,4-Trimethyl-5-phenylhexane	133—135 (23) 106—107 (4) **		1.5088 1.5050	0.8970 0.8936	68.00 67.82	67.84	88.26 88.10	11.82 11.88	88.16	11.84
2,4,4-Trimethyl-5-cyclohexylhexane	129 (15)	—84 (glass)	1.4636	0.8442	68.72	68.85	85.68	14.30	85.63	14.37
1-Methyl-4-(1,1,3,3-tetramethylbutyl)--benzene	111—113 (9)		1.5094	0.8934	68.34	68.22	88.36	11.62	88.16	11.84
1-Methyl-4-(1,1,3,3-tetramethylbutyl)--cyclohexane	102 (5)	—72 (glass)	1.4580	0.8366	68.63	69.08	85.75	14.37	85.63	14.37

* Calculated by V. M. Tatevsky's method [10].
** Repeat values for hydrocarbons prepared in heptane.

*Calculated by V. M. Tatevsky's method [10].
**Repeat values for hydrocarbons prepared in heptane.

The higher yields resulting from replacement of ether (in preparing the Grignard reagent) by heptane are evidently due to the more considerable cleavage of HCl when using ether owing to formation of oxonium compounds. Here we should note that we performed the experiments in heptane at room temperature. The result of synthesis 5 is of particular interest; this could not generally be realized in ether.

The prepared alkylbenzenes were subjected to hydrogenation over Ni in an autoclave at 180-200° and an initial pressure of 130 atm to give the corresponding alkylcyclohexanes. The properties of the alkylbenzenes and alkylcyclohexanes are presented in Table 2.

EXPERIMENTAL

1. Synthesis of 1-methyl-4-(1,1,3-trimethylbutyl)-benzene. p-Bromotoluene was prepared by bromination of toluene in the cold in presence of a catalyst (iron filings). 1-Chloro-2,4-dimethypentane was prepared by hydrogenation at 0° of 2,4-dimethylpentanol-2, obtained by the Grignard reaction from methyl magnesium bromide and methyl isobutyl ketone.

The chloro compound had b.p. 46.5° at 41 mm, n_D^{20} 1.4180; d_4^{20} 0.8554; literature [4]: b.p. 33-34° at 20 mm, n_D^{15} 1.4239.

Found %: Cl 25.93. $C_7H_{15}Cl$. Calculated %: Cl 26.37.

To the Grignard reagent prepared from 24.5 g of magnesium and 172 g of p-bromotoluene in ether was added dropwise 137 g of 2-chloro-2,4-dimethylpentane in 150 ml of ether, after which the reaction mixture was stirred at room temperature until the Gilman test was negative (6 hours). Decomposition was effected with 5% HCl. The ether layer was separated and the solvent was driven off. Two distillations of the residue over metallic sodium gave 19 g of 1-methyl-4-(1,1,3-trimethylbutyl)-benzene, which was hydrogenated to 1-methyl-4-(1,1,3-trimethylbutyl)-cyclohexane.

2. Synthesis of 1,2-dimethyl-4-(1,1,3-trimethylbutyl)-benzene. 4-Bromo-o-xylene was prepared [5] by catalytic bromination of o-xylene which had been purified by recrystallization of its Na-sulfonate [6]. 12.5 g of magnesium, 93 g of 4-bromo-o-xylene and 69 g of 2-chloro-2,4-dimethylpentane in ether were reacted as described above and gave 4.1 g of 1,2-dimethyl-4-(1,1,3-trimethylbutyl)-benzene, which was hydrogenated to 1,2-dimethyl-4-(1,1,3-trimethylbutyl)-cyclohexane.

3. Synthesis of 1,3-dimethyl-4-(1,1,3-trimethylbutyl)-benzene. 4-Bromo-m-xylene was prepared by catalytic bromination of m-xylene [5] which was purified [7] by treatment with dilute nitric acid. Using the above procedure, 12.5 g of magnesium, 93 g of 4-bromo-m-xylene and 69 g of 2-chloro-2,4-dimethylpentane in ether gave 5.1 g of 1,3-dimethyl-4-(1,1,3-trimethylbutyl)-benzene.

In another experiment, after preparation of the Grignard reagent from 12.5 g of magnesium and 93 g of 4-bromo-m-xylene, the ether was driven off, 200 ml of dry heptane was charged into the reaction flask, and a solution of 69 g of 2-chloro-2,4-dimethylpentane in 100 ml of heptane was added at room temperature. 12 g of a hydrocarbon was obtained whose properties agreed with those of 1,3-dimethyl-4-(1,1,3-trimethylbutyl)-benzene prepared in ether. The alkylbenzene was hydrogenated to 1,3-dimethyl-4-(1,1,3-trimethylbutyl)-cyclohexane.

4. Synthesis of 2,4,4-trimethyl-5-phenylhexane. α-Bromoethylbenzene was prepared [8] by saturating an ethereal solution of styrene with dry HBr at 0° (the β-isomer is not formed under these conditions).

B.p. 71° at 6 mm, n_D^{20} 1.5482, d_4^{20} 1.3490. Literature [8]: b.p. 77-79° at 10 mm, 63-64° at 2 mm, n_D^{20} 1.5470, d_4^{20} 1.3472.

Found %: Br 42.60. C_8H_9Br. Calculated %: Br 43.18.

The Grignard reagent was prepared from 93 g of α-bromoethylbenzene and 73.5 g of magnesium in ether [8]. The further procedure was similar to that described above. 8 g of 2,4,4-trimethyl-5-phenylhexane was obtained; this was hydrogenated to 2,4,4-trimethyl-5-cyclohexylhexane. Replacement of ether by heptane increased the yield of 2,4,4-triethyl-5-phenylhexane fourfold (to 16%).

5. Synthesis of 1-methyl-4-(1,1,1,3-tetramethylbutyl)-benzene. 2-Chloro-2,4,4-trimethylpentane was prepared by saturation of 2,4,4-trimethylpentene-3 with dry HCl at −15°; the latter hydrocarbon had been prepared by fractionation of diisobutylene. The structure of the olefin (fraction with b.p. 103-105°, n_D^{20} 1.4167-1.4170, d_4^{20} 0.7311) as 2,4,4-trimethylpentene-3 was confirmed by oxidation.

Chloro compound: b.p. 54° at 20 mm, n_D^{20} 1.4382, d_4^{20} 0.8914. Literature [9]: b.p. 40° at 13 mm, d_0^0 0.8891.

Found %: Cl 23.23. $C_9H_{17}Cl$. Calculated %: Cl 23.84.

The product of normal condensation — 1-methyl-4-(1,1,3,3-tetramethylbutyl)-benzene — could not be isolated when the synthesis was attempted by the above-described procedure in ether. After replacement of ether by heptane, 12 g of magnesium, 86 g of p-bromotoluene and 75 g of 2-chloro-2,4,4-trimethylpentane gave 8.3 g of 1-methyl-4-(1,1,3,3-tetramethylbutyl)-benzene, which was hydrogenated to the corresponding alkylcyclohexane.

In all of the experiments, the normal product of condensation was accompanied by a large quantity (up to 70%) of olefins due to cleavage of HCl, also by aromatic hydrocarbon (product of reduction of the Grignard reagent). In synthesis 4, in addition, about 30% of meso-2,3-diphenylbutane was obtained; m.p. 123-125°.

SUMMARY

It was shown that the Würtz-Fitting condensation of tertiary alkyl halides with bromobenzene and its homologs, with replacement of ether by heptane in the second step, enables the yield of alkylbenzene to be increased several-fold.

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** In Russian.

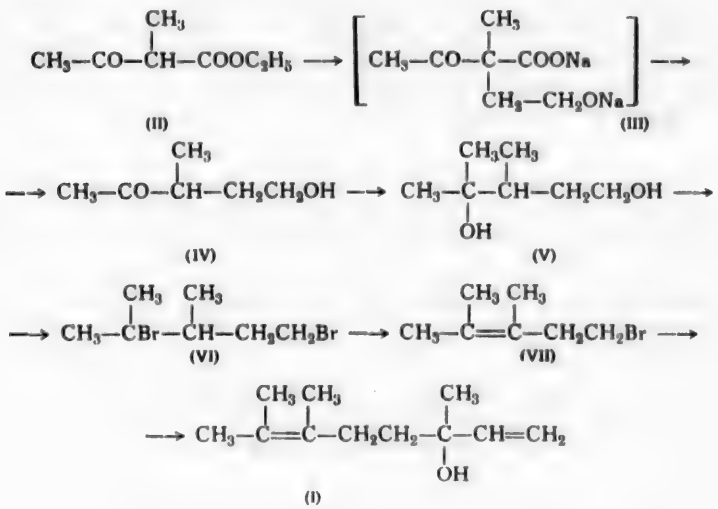
SYNTHESIS OF 2,3,6-TRIMETHYLOCTADIEN-2,7-OL-6 (3-METHYLLINALOOL)

I. K. Sarycheva, G. A. Vorobyeva, L. G. Kucheryavenko and N. A. Preobrazhensky

In published methods for synthesis of irones, the usual principal intermediate products are 1-bromo-2,3-dimethylbutene-2 and 2,3-dimethylhepten-2-one-6, which are then converted into pseudoirone via 3-methyllinalool and 3-methylcitral [1]. Replacement of 2,3-dimethylhepten-2-one-6 by 2-methyl-3-methylheptanone-6 [2] did not introduce any essential changes into the previously advanced schemes but provided a new source of raw material. In this connection it was of interest to develop from available compounds another route to the $CH_3-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_2$ grouping which is the basis of a series of intermediates in syntheses of irones.

In the present work we describe the synthesis of 3-methylinalool (I), starting from methylacetoacetic ester.

Scheme I

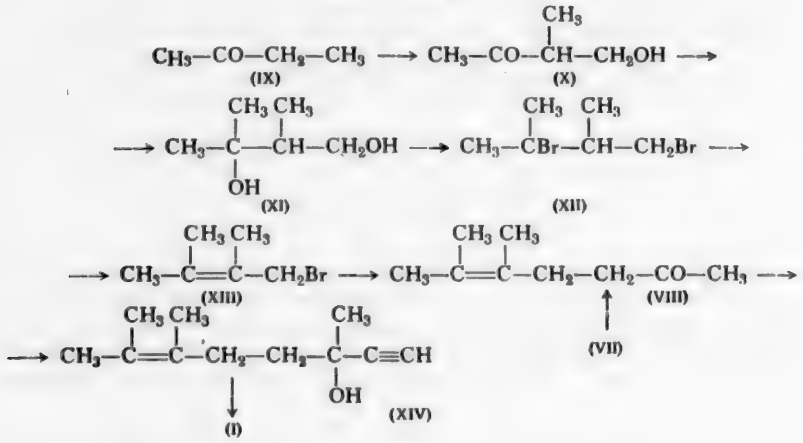


Reaction of methylacetoacetic ester (II) [3] with ethylene oxide in an alcoholic sodium ethoxide medium gave 3-methylpentane-4-ol-1 (IV) [4]. An intermediate stage in this reaction was presumably the formation of the sodium salt of acid (III) which on acidification underwent hydrolytic cleavage to 3-methylpentanone-4-ol-1 (IV). Reaction of (IV) with methyl magnesium iodide led to formation of 2,3-dimethylpentanediol-2,5 (V), which by treatment with phosphorus tribromide and pyridine was transformed into 2,5-dibromo-2,3-dimethylpentane (VI), and then into 5-bromo-2,3-dimethylpentene-2 (VII). Condensation of (VII) with methyl vinyl

ketone in presence of lithium (experiment 1) gave 3-methyllinalool (I) in a yield of 14.1%; replacement of lithium by magnesium (experiment 2) enabled the yield of (I) to be raised to 37%. 3-Methyllinalool (I) was characterized by its physicochemical constants and by its infrared absorption spectrum (see diagram). •

3-Methyllinalool (I) was also synthesized from 2,3-dimethylhepten-2-one-6 (VIII) which in turn was obtained by new methods.

Scheme 2



For the preparation of 2,3-dimethylhepten-2-one-6 (VIII), 5-bromo-2,3-dimethylheptene-2 (VII), which is used in the synthesis of 3-methyllinalool (scheme 1), was brought into reaction with acetic anhydride and magnesium (yield 38.2%) [5]. In addition, 2,3-dimethylhepten-2-one-6 (VIII) was synthesized from 2-methylbutanone-3-ol-1 (X); the latter was converted by a series of reactions into 1-bromo-2,3-dimethylbutene-2 (XIII), using the procedure proposed for synthesis of 5-bromo-2,3-dimethylpentene-2 (VII) (scheme 1). The transition from 1-bromo-2,3-dimethylbutene-2 (XIII) to 2,3-dimethylhepten -2-one-6 (VIII) and from the latter to 3-methyllinalool (I) was realized via 2,3,6-trimethylocten-2-yn-7-ol-6 [6].

EXPERIMENTAL

1. 3-Methylpentanon-4-ol-1; γ-methyl-γ-acetopropyl alcohol (IV). To sodium ethoxide, prepared from 388.8 g (8.45 moles) of ethyl alcohol and 29.8 g (1.30 g-atoms) of sodium, was added 188 g (1.30 moles) of freshly distilled methylacetoacetic ester (b.p. 79.2-80.1° at 24 mm) [3] in the course of 30 minutes with vigorous stirring; the mixture was then left for 45 minutes at room temperature. To the reaction mass, cooled to −10°, was then added a solution of 100 g (2.27 moles) of ethylene oxide in 250 ml of anhydrous ethyl alcohol (also previously cooled to −10°) in the course of 15 minutes; the mixture was then left for 2 hours in a freezing mixture. The gradually thickening solution was stirred at room temperature for 48 hours, acidified with 33% acetic acid (pH 6.5), and extracted with 500 ml ether and 600 ml of ethyl acetate. The combined extracts were dried with sodium sulfate. After removal of the solvent, the residue was distilled in vacuo to give 87.4 g (57.7%) of product. B. p. 83-85.7° at 20 mm.

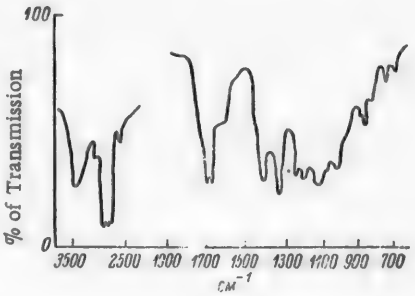
2. 2,3-Dimethylpentanediol-2,5 (V). A solution of 40 g (0.34 mole) of (IV) was added dropwise with stirring in the course of 30 minutes to methyl magnesium iodide (cooled to −5°) prepared from 34.04 g (1.40 atoms) of magnesium turnings and 200 g (1.40 moles) of methyl iodide in 200 ml of dry ether. After standing for 24 hours at room temperature followed by 2 hours at 50-60°, the reaction mass was cooled to 0° and 70 ml of iced water was run into it in the course of 30 minutes; thereupon, while still being cooled, the mass was neutralized with 20% acetic acid, 5 g of sodium thiosulfate was added, and the mixture was stirred for 5 minutes. The

• Spectral measurements were made with the IKS-2 (double-beam) spectrometer, using a Glo-bar as source of light. The cells were plates of sodium chloride (700-2000 cm^{-1}) and lithium fluoride (2200-4000 cm^{-1}). The slit was automatically adjusted.

upper ethereal layer was separated, and the lower layer was saturated with 100 g of ammonium chloride and extracted with 300 ml of ether and 400 ml of ethyl acetate. The combined extracts together with the upper layer were dried with sodium sulfate. The solvents were driven off and the residue distilled. Yield 24.7 g (54.2%).

B. p. 96.3-97° at 10 mm, n_D^{20} 1.4502, d_4^{20} 0.9528, MR_D 37.25; calc. 37.58.

Found %: C 63.33, 63.37; H 12.36, 12.27. $C_7H_{16}O_2$. Calculated %: C 63.60; H 12.20.



Infrared absorption spectrum of 3-methyllinalool.

3. 2,5-Dibromo-2,3-dimethylpentane (VI). 43 g (0.16 mole) of phosphorus tribromide was added dropwise over a period of 45 minutes to a solution of 21 g (0.16 mole) of (V) in 100 ml of dry benzene (cooled to 0°). The reaction mass was stirred for 3 hours at room temperature, cooled to −5° and treated with 40 ml of iced water. The upper benzene layer was separated and the lower layer extracted with 250 ml of benzene. The combined benzene extract and upper layer were washed with a saturated aqueous solution of sodium bicarbonate and dried with sodium sulfate. After removal of the solvent, the residue was distilled. Yield 20.8 g (50.7%).

B. p. 98-100° at 10 mm, n_D^{20} 1.5051, d_4^{20} 1.5170, MR_D 50.46. $C_7H_{14}Br_2$. Calculated MR_D 50.06.

Found %: C 32.92, 33.13; H 5.49, 5.63. $C_7H_{14}Br_2$. Calculated %: C 32.59; H 5.47.

4. 5-Bromo-2,3-dimethylpentene-2 (VII). A mixture of 20.8 g (0.08 mole) of (VI) and 6.6 g (0.08 mole) of dry pyridine was heated at 80° in a low vacuum (100 mm) for 20 minutes; a precipitate was formed. Without change of pressure, the temperature of the reaction mass was raised to 90° and held for about 45 minutes. After cooling to room temperature, the reaction product was poured into 10 ml of iced water and extracted with 100 ml of ether. The ethereal extract was washed with 50 ml of sulfuric acid (d_4^{20} 1.03), then with 25 ml of iced water and dried with sodium sulfate. After removal of the solvent, the residue was distilled. Yield 10.4 g (72.8%).

B. p. 63.5-65° at 9 mm, n_D^{20} 1.4805, d_4^{20} 1.1921, MR_D 42.22. $C_7H_{13}Br$. Calculated MR_D 41.82.

5. 2,3,6-Trimethyldecadien-2,7-ol-6 (3-methyllinalool) (I). Experiment 1. To 0.47 g (0.067 atom) of lithium, covered with 20 ml of dry ether, was added a solution of 5.2 g (0.67 mole) of (VII) in 15 ml of dry ether dropwise in the course of 1 hour. The reaction mass was heated at the boil for 2 hours, after which it was cooled to 0°; addition was made dropwise of a solution of 2.05 g (0.067 mole) of methyl vinyl ketone in 20 ml of dry ether. A grey-green precipitate came down. The mixture was heated for an hour on a water bath and held for 24 hours at room temperature. After removal of unreacted lithium, the mass was treated with 10 ml of iced water. The upper ethereal layer was separated and the lower layer was extracted with 250 ml of ether; the combined extracts were dried with sodium sulfate; after removal of the solvent, the residue was distilled. Yield 0.65 g (14.1%).

B p. 95.2-98.2° at 10 mm, n_D^{20} 1.4612, d_4^{20} 0.8606, MR_D 53.48. $C_{11}H_{20}O$. Calculated MR_D 53.59.

Found %: C 78.81, 78.56; H 11.87, 12.12. $C_{11}H_{20}O$. Calculated %: C 78.50; H 11.94.

Experiment 2. To 0.56 g (0.023 mole) of magnesium turnings covered with 5 ml of dry ether, was added a few drops of ethyl bromide; when the reaction mass began to turn cloudy on boiling, a solution of 4 g (0.023 mole) of (VII) in 10 ml of ether was run in over a period of 20 minutes. The resultant grey mass was heated for 2 hours; it was then cooled to 0° and a solution of 1.58 g (0.023 mole) of freshly distilled methylvinylketone (b. p. 79.5-80° at 759 mm) in 10 ml of ether was introduced dropwise; a yellowish-green precipitate appeared. After standing for 24 hours at room temperature, the reaction mass was treated with 12 ml of iced water and 18 ml of 15% acetic acid. The upper ethereal layer was separated, the lower layer was extracted with 100 ml of ether, the combined ethereal extracts were neutralized with a saturated aqueous solution of sodium bicarbonate, and dried with sodium sulfate. After driving off the solvent, the residue was distilled. Yield 1.4 g (37%).

B. p. 93-95.4° at 8 mm, n_D^{20} 1.4642, d_4^{20} 0.8763, MR_D 53.09. $C_{11}H_{20}OF_2$. Calculated MR_D 53.59.

Found %: C 78.84; H 11.79. $C_{11}H_{20}O$. Calculated %: C 78.50; H 11.94.

Infrared spectrum: 3450 (very strong), 3080 (weak), 2980 (strong), 2925 (strong), 2860 (strong), 2750 (weak), 1700 (very strong), 1690 (very strong), 1635 (medium), 1435 (strong), 1350 (very strong), 1260 (medium), 1220 (medium), 1140 (strong), 1030 (medium), 915 (weak), 885 (medium), 840 (weak), 750 (medium).

6. 2,3-Dimethylhepten-2-one-6 (VIII). To a solution (cooled to −70°) of 4.7 g (0.046 mole) of acetic anhydride in 10 ml of dry ether was added, dropwise over a period of 15 minutes, a Grignard reagent prepared from 0.56 g (0.023 atom) of magnesium and 4 g (0.023 mole) of (VII) in 10 ml of dry ether. The reaction mass was carefully stirred for 2 hours at −65°, after which the temperature of the reaction mass was raised to room temperature; the mass was treated with 20 ml of a saturated aqueous solution of ammonium chloride and 10 ml of 10% aqueous sodium hydroxide. The upper layer was separated and the lower layer extracted with 120 ml of ether. The combined extracts were dried with sodium sulfate. The residue, after removal of solvent, was distilled. Yield 1.21 g (38.2%).

B.p. 74-76° at 10 mm, n_D^{20} 1.4500, d_4^{20} 0.8707, MR_D 43.17. $C_9H_{16}OF$. Calculated MR_D 43.31.

Found %: C 77.39, 77.00; H 11.50, 11.77. $C_9H_{16}O$. Calculated %: C 77.11; H 11.50.

2,4-Dinitrophenylhydrazone. M. p. 97-98.5° (from ethyl alcohol).

Found %: N 17.79, 17.55. $C_{15}H_{20}O_4N_4$. Calculated %: N 17.50.

7. 2-Methylbutanon-3-ol-1 (X). Into a mixture of 150.9 g of freshly distilled (b.p. 77-78° at 735 mm) methyl ethyl ketone (IX) and 33 ml of aqueous solution of formaldehyde (d_4^{20} 1.102) at room temperature was stirred dropwise 6 ml of 2% aqueous solution of sodium hydroxide (pH 7.5). The temperature of the reaction mass was held at 29-30° for 3 hours; the mass (after addition of 0.5 g of hydroquinone) was left for 12 hours at room temperature. After a low-boiling fraction had been distilled off, the residue was distilled in vacuo. Yield 17 g (42.1%).

B. p. 97-97.5° at 26 mm, n_D^{20} 1.4308, d_4^{20} 0.9982, MR_D 26.44; calc. 26.82.

Found %: C 58.68, 58.73; H 9.62, 9.49. $C_5H_{10}O_2$. Calculated %: C 58.83; H 9.87.

8. 2,3-Dimethylbutanediol-2,4 (XI). To methyl magnesium iodide (cooled to −5°), prepared from 24.3 g (1 atom) of magnesium turnings and 142 g (1 mole) of methyl iodide in 200 ml of dry ether, was added 42 g (0.41 mole) of (X) dropwise in the course of 25 minutes; the mass was stood for 24 hours at room temperature. It was then heated at the boil for 1 hour and (after cooling to 0°) 50 ml of iced water was added. The mixture was neutralized with 20% acetic acid and stirred with 5 g of sodium thiosulfate. The upper ethereal layer was separated and the lower layer was saturated with 100 g of ammonium chloride and extracted with 300 ml of ether and 250 ml of ethyl acetate. The combined extracts were dried with sodium sulfate. After removal of the solvents, the residue was distilled. Yield 18.4 g (37.87%).

B. p. 95-95.5° at 7 mm, n_D^{20} 1.4489, d_4^{20} 0.9980; MR_D 31.77; calc. 32.96.

Found %: C 61.27, 60.85; H 11.80, 11.76. $C_6H_{14}O_2$. Calculated %: C 60.95; H 11.93.

9. 2,4-Dibromo-2,3-dimethylbutane (XII). 33 g (0.127 mole) of phosphorus tribromide was added dropwise in the course of 45 minutes to a solution (cooled to 0°) of 15 g (0.127 mole) of (XI) in 30 ml of dry benzene. The reaction mass was stirred for 3 hours at room temperature, then cooled to −5° and treated with 20 ml of iced water. The upper benzene layer was separated and the lower layer extracted with 250 ml of benzene. The combined extracts were washed with saturated aqueous sodium bicarbonate solution and dried with sodium sulfate. After the solvent had been distilled off, the residue was distilled. Yield 16.2 g (52.4%). B. p. 82.5-83° at 20 mm.

Found %: C 30.15; H 5.40. $C_6H_{12}Br_2$. Calculated %: C 29.53; H 4.96.

10. 1-Bromo-2,3-dimethylbutene-2 (XIII). 1.15 g (0.014 mole) of dry pyridine was run into 3.5 g (0.014 mole) of (XII) and the mixture heated to 75° in a low vacuum (200 mm) for 20 minutes; a voluminous precipitate appeared. Without alteration of pressure, the temperature of the reaction mass was raised to 80° and held for about 1 hour. After cooling to room temperature, the reaction product was run into 10 ml of iced water and

extracted with 100 ml of ether. The ethereal extract was washed with 30 ml of sulfuric acid (d_4^{20} 1.03) and dried with sodium sulfate. The residue, following distillation of the solvent, was distilled. A colorless liquid, rapidly darkened in the light, with strong lachrymatory action. Yield 1.55 g (66.24%).

B. p. 69.9-73° at 50° mm, n_D^{20} 1.4942, d_4^{20} 1.2662, MR_D 37.63. $C_6H_{11}BrF$. Calculated MR_D 37.21.

SUMMARY

1. 3-Methyllinalool was synthesized by a series of reactions.

2. New methods of preparation of 1-bromo-2,3-dimethylbutene-2 and 2,3-dimethylhepten-2-one-6 were developed.

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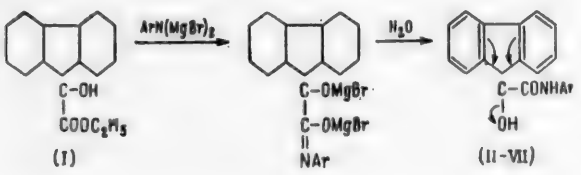
REACTIONS OF MAGNESYL AMINES

II. SYNTHESIS AND PROPERTIES OF ARYLAMIDES OF 9-HYDROXYFLUORENE-9-CARBOXYLIC ACID

P. A. Petyunin and I. S. Berdinsky

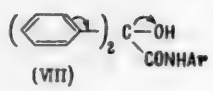
As is well known, the reaction of aromatic amines with acids or esters is one of the principal methods of preparation of arylamides of carboxylic acids; these methods, however, are not always satisfactory. Thus, for example, Liebig [1] heated benzilic acid with aromatic amines and obtained, apart from arylamides of benzilic acid, a series of high-molecular substances of unknown structure. Reaction between aniline and ethyl β,β-diphenyl-β-hydroxypropionate did not lead to the desired results [2]. In such cases the synthesis of arylamides can be realized by the use of "magnesylamines" [2, 3].

We found it necessary to synthesize arylamides of 9-hydroxyfluorene-9-carboxylic acid. Since the latter, like the above-mentioned acids, contain a mobile hydroxyl group, its arylamides were synthesized with the help of dimagnesylamines. The reaction goes as follows:



The arylamides were obtained in yields of 77-95%. Of the 6 compounds that we obtained, only the anilide of 9-hydroxyfluorene-9-carboxylic acid has been described in the literature; this had been prepared by reaction of aniline with 9-chlorofluorene-9-carboxylic acid chloride and subsequent replacement of chlorine by hydroxyl [4].

In analogy with the arylamides of benzilic acid (VIII), we could expect that our arylamides of 9-hydroxyfluorene-9-carboxylic acid (II-VII) would exhibit the property of halochromism. In this acidolysis reaction, arylamides manifest basic properties which are accounted for by conjugation of the π-electrons of the benzene rings with ungeneralized electrons of the hydroxyl oxygen.



(VIII)

Experiments showed that in the arylamides (II-VII) the basic character is very weakly developed and even in a medium of concentrated sulfuric acid they do not give colored solutions. This behavior indicates that the above-mentioned conjugation is not so strongly marked in these compounds as in (VIII), probably due to the developed tendency of the 5-membered ring of the fluorene system to form an aromatic sextet [5].

EXPERIMENTAL

Methyl ester of 9-hydroxyfluorene-9-carboxylic acid (I). To a solution of 5 g of 9-hydroxyfluorene-9-carboxylic acid in 50 ml of methanol was added 5 ml of concentrated sulfuric acid; heating was carried out

on a water bath for 3 hours. The greater part of the alcohol was distilled off, the residue was neutralized with sodium carbonate, and the resultant precipitate was crystallized from alcohol. Yield 4.3 g (81.1%). Prisms with m.p. 158-159°. The literature gives m. p. 158-160° [6].

Anilide of 9-hydroxyfluorene-9-carboxylic acid (II). To N,N-bis-(magnesium bromide) aniline, prepared from 1.91 g of ethyl bromide, 0.43 g of magnesium and 0.82 g of aniline in 10 ml of ether, was added a solution of 1.4 g of (I) in 10 ml of ether; the mixture was heated for 30 minutes on a water bath and decomposed with dilute hydrochloric acid. The product of reaction was isolated from the ethereal layer. It is soluble in alcohol, ether and toluene. Yield 1.5 g (83.3%). Needles (from toluene) with m.p. 201-202°. The literature reports m.p. 201-202° [4].

p-Toluidide of 9-hydroxyfluorene-9-carboxylic acid (III). Starting substances: 2.2 g of ethyl bromide, 0.5 g of magnesium, 1.6 g of p-toluidine and 2.4 g of (I). Yield 3 g (95.1%). Sparingly soluble in ether, alcohol and chloroform, easily soluble in toluene, benzene and glacial acetic acid. Needles (from glacial acetic acid) with m.p. 207-208.5°.

Found %: N 4.33, 4.42. $C_{21}H_{17}O_2N$. Calculated % N 4.44.

p-Anisidide of 9-hydroxyfluorene-9-carboxylic acid (IV). Reaction was carried out between the dimagnesylamine, prepared from 3.3 g of ethyl bromide, 0.75 g of magnesium and 1.8 g of p-anisidine, and 2.4 g of (I). Yield 2.57 g (78%). Sparingly soluble in alcohol, toluene, glacial acetic acid and carbon tetrachloride. Needles (from toluene) with m. p. 208-209.5°.

Found %: Found %: N 4.56, 4.35. $C_{21}H_{17}O_3N$. Calculated %: N 4.35.

p-Chloroanilide of 9-hydroxyfluorene-9-carboxylic acid (V). Starting substances: 2.75 g of ethyl bromide, 0.63 g of magnesium, 1.58 g of p-chloroaniline and 2 g of (I). Yield 2.3 g (85.2%). Good solubility in acetic acid, sparingly soluble in alcohol, toluene and dioxan Prisms (from toluene) with m.p. 224-226°.

Found %: N 4.19, 4.48. $C_{20}H_{14}O_2NCl$. Calculated %: N 4.18.

p-Bromoanilide of 9-hydroxyfluorene-9-carboxylic acid (VI). Starting substances: 2.5 g of ethyl bromide, 0.56 g of magnesium, 1.2 g of p-bromoaniline and 1.8 g of (I). Yield 2.37 g (83.1%). Readily soluble in acetic acid, sparingly in alcohol and toluene. Needles (from toluene) with m.p. 220-222°.

Found %: N 3.55, 3.53. $C_{20}H_{14}O_2NBr$. Calculated %: N 3.68.

β-Naphthalide of 9-hydroxyfluorene-9-carboxylic acid (VII). Starting substances: 2.5 g of ethyl bromide, 0.56 g of magnesium, 1.6 g of β-naphthylamine and 1.8 g of (I). Yield 2.1 g (77.8%). Sparingly soluble in ether, alcohol and toluene, more easily in glacial acetic acid. Prisms (from toluene) with m. p. 220-221°.

Found %: N 4.19, 4.29. $C_{24}H_{17}O_2N$. Calculated % N 3.90.

SUMMARY

1. A convenient preparative method for arylamides of 9-hydroxyfluorene-9-carboxylic acid was developed.

2. A series of previously undescribed arylamides of 9-hydroxyfluorene-9-carboxylic acid was prepared and their properties studied.

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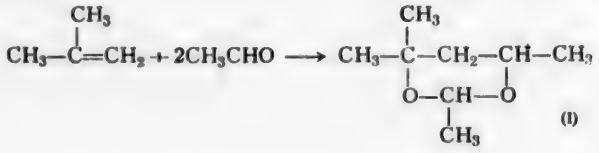
**Russian translation.

SYNTHESIS OF METHYLPENTADIENE ON THE BASIS OF ISOBUTYLENE AND ACETALDEHYDE

M. I. Farberov and K. A. Machtina

Methylpentadiene is not easily accessible on the technical scale. The sole method of possible industrial value starts from acetone and involves a number of steps [1]. Methylpentadiene is, however, of definite industrial interest since its polymers and copolymers possess valuable properties [2].

Over a number of years we have studied reactions of olefins with aldehydes and possible methods of utilization of these reactions. The main product of reaction of isobutylene with acetaldehyde in an aqueous medium in presence of 1-2% sulfuric acid is 2,4,4,6-tetramethyldioxan -1,3 (I) [3]. The yield is 90% on the reacted aldehyde.



According to the literature, alkyldioxans are susceptible to cleavage with formation of dienes of the butadiene series when passed over catalysts [4].

In the present work it was shown that on passing the alkyldioxan (I) in admixture with steam at 300-325° over a phosphate type of catalyst, methylpentadiene is obtained in a yield of up to 75 mole-% on the tetramethyldioxan decomposed.

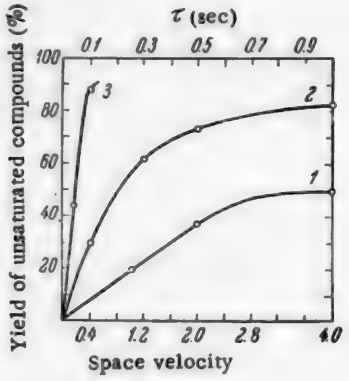


Fig. 1. Influence of temperature and space velocity on the yield of unsaturated compounds during catalytic cleavage of tetramethyldioxan. 1) 275°, 2) 300°, 3) 325°.

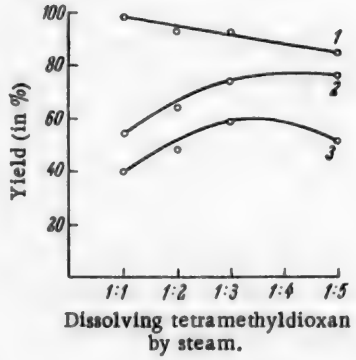
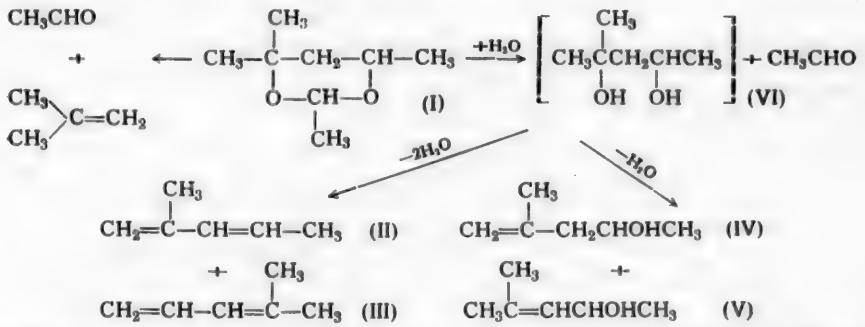


Fig. 2. Influence of dilution with steam on the catalytic cleavage of tetramethyldioxan at 325° and τ = 0.5 sec. 1) Total conversion; 2) yield of unsaturated compounds reckoned on the tetramethyldioxan introduced; 3) yield of methylpentadiene reckoned on tetramethyldioxan introduced.

Formation of two isomeric dienes is possible as a result of cleavage of (I) in presence of a catalyst: 2-methylpentadiene-1,3 (II) and 4-methylpentadiene-1,3 (III); the properties of the two isomers are very similar. Quantitative determination of the composition of the mixture of isomers is based on their difference in behavior toward maleic anhydride: (II) forms the normal adduct with maleic anhydride but (III) forms a copolymer. The susceptibility of (III) to polymerization can be suppressed by inhibitors, and it can be completely separated from (II)[5]. Determinations on this basis showed that the methylpentadiene contained 45% of (II) and 55% of (III).

In addition to methylpentadiene, catalytic cleavage of (I) gives small quantities of a mixture of two isomeric unsaturated alcohols – 4-methyl-4-pentenol-2 (IV) and 4-methyl-3-pentenol-2 (V). There is also breakdown of (I) to the original acetaldehyde and isobutylene. These transformations are represented by the following equations:



We consider the following mechanism of the catalytic cleavage of tetramethyldioxan (I) to be probable: Water hydrolyzes (I) at the surface of the catalyst with formation of 2-methylpentadiol-2,4 (VI). In the instant of formation, (VI) dehydrates with loss of one or two molecules of water to form a mixture of isomeric unsaturated alcohols (IV) and (V) and a mixture of dienes (II) and (III) respectively. In the former case, a hydroxyl group is split off only at the tertiary carbon atom.

In the present work we also studied the influence of the reaction conditions on the process of catalytic cleavage of the dioxan (I). The experimental results were evaluated on the basis of data for the total conversion, yields of unsaturates and yield of dienes reckoned on the amount of (I) introduced into the reaction.

Curves of the influence of temperature and reciprocal space velocity (space vel.$^{-1}$) on the total yield of unsaturated compounds are plotted in Fig. 1; the effect of dilution with steam is plotted in Fig. 2.

A quantitative relation between rate of catalytic cleavage of (I) and temperature can be found by a graphical treatment of the curves of total yield of unsaturated compounds versus temperature and versus the conventional time of contact (τ) at constant degree of conversion (Fig. 1). The plot of log v versus temperature (Fig. 3) constructed in this manner is a straight line (mean reaction rate $v = y/\tau$, where y is the degree of conversion, equal to 30%). The apparent energy of activation calculated from the slope of the plot is 33,900 cal/mole.

The table contains data for one of the typical material-balance experiments on catalytic cleavage of tetramethyldioxan (I). Experimental conditions: temperature 325°, space velocity 2.63, dilution with steam 1:3, amount of substance passed through 47.67 g of (I).

EXPERIMENTAL*

Apparatus and procedure. Experiments on cleavage of (I) were undertaken in a block electric furnace containing a channel for the quartz reaction tube (d. 17 mm, length 900 mm). The temperature was held constant

* With participation of student Ya. N. Prokofyev.

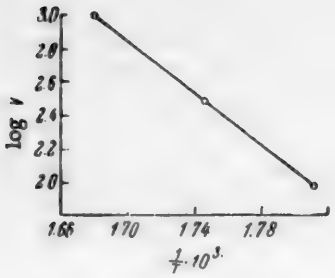


Fig. 3. Relation between reaction velocity and temperature.

to 2° with the help of an autotransformer. Water and (I) were admitted from small burets. A mixture of (I) and water passed through a mixing device into a vaporizer where the vapors were brought to the experimental temperature, which was measured by thermocouples at the top and bottom of the catalyst bed. The catalyzed gas passed through a condenser in which a considerable proportion condensed, and this was collected in a receiving flask. Uncondensed gas entered a gasholder.

The condensate was fractionated in a 38-plate column and gave the following fractions; 1) 60-80° (methylpentadiene and water); 2) 86-96° (mainly 92-93°). After removal of the water layer, the first fraction was analyzed for its content of dienes by reaction with maleic anhydride in sealed ampoules [6]. The unchanged dioxan (I) in the second fraction was determined by hydrolysis in presence of salts of hydroxylamine [7].

The gas was analyzed for its content of unsaturates and carbon dioxide in the Orsat apparatus, while dienic hydrocarbons were determined in the Bushmarin apparatus [8].

Products of reaction	Yield (in g)	Yield (in mole-%)	
		on (I) introduced	on (I) decomposed
Methylpentadiene	18.60	68.6	74.4
Isobutylene	3.28	17.7	19.2
Butylenes and propylene	0.27	1.4	1.5
Carbon on catalyst	0.05	0.2	0.2
Unchanged (I)	2.30	4.8	–
Methylpentenol	1.01	3.0	–
Resin and losses	2.16	4.3	4.7
	27.67	100.0	100.0

The conventional time of contact was calculated from the formula

$$\tau = \frac{v_c \cdot 273 \cdot P}{v_g \cdot T \cdot 760},$$

where v_c is the volume of the catalyst (in ml), assumed to be 65% of the bulk volume, v_g is the volume of gases reaching the catalyst zone (in ml/sec), P is the pressure (mm), and T is the absolute temperature.

The initial 2,4,4,6-tetramethyldioxan -1,3 had b.p. 139-141°, d_4^{20} 0.9039, n_D^{20} 1.4192 [3].

Catalyst. A phosphate catalyst for selective cleavage of alkyl-1,3-dioxans to dienes was used. The catalyst was regenerated after each experiment. It was tested for activity under standard conditions periodically.

The mixture of isomeric methylpentadienes (II) and (III) had:

B. p. 75.5° (760 mm), d_4^{20} 0.7215, n_D^{20} 1.4462, MR_D 30.309; calc. 30.07.

Literature data for mixtures of isomers (II) and (III) [9]: b. p. 72.5-75.5°, n_D^{20} 1.4474.

Quantitative determination of (II) and (III) was performed by a slight modification of the method described in [5]. An ampoule containing an exactly weighed quantity (0.5-0.7 g) of methylpentadiene was introduced into a large cooled ampoule containing a weighed quantity of maleic anhydride in 5-7 ml of toluene; after keeping at room temperature, the large ampoule was opened and the toluene and unreacted (III) were sucked out (in vacuum) until the weight was constant. The melting point of the adduct of (II) with maleic anhydride is 57.8-59.1°; the literature gives 57° [5].

A mixture of isomeric methylpentenols (IV) and (V) was isolated from the undecomposed dioxan (I). After drying with potassium carbonate, the (I) was fractionated in a column. The 128-130° fraction, assumed to be a mixture of (IV) and (V), was refractionated in a microcolumn, after which it had b.p. 128-130°, n_D^{20} 1.4275, in agreement with the literature [10].

Determination of the percent content of alcohol in the fraction by acetylation and on the basis of the degree of unsaturation (bromide-bromate method) gave results in good agreement (75.5 and 76.4% respectively). Methylpentenol acetate was also prepared:

B. p. 142-143° (742 mm), n_D^{20} 1.4160, d_4^{20} 0.8852, MR_D 40.2; calc. 40.48.

Literature data for the acetate of (IV): b. p. 150.1° (763 mm), n_D^{20} 1.4167, d_4^{20} 0.8852 [10].

SUMMARY

Catalytic cleavage of 2,4,4,6-tetramethyl-1,3-dioxan gave a mixture of isomeric methylpentadienes in a yield of 75%. Small quantities of isomeric methylpentenols were formed at the same time.

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DERIVATIVES OF HEXAMETHYLENEIMINE

II. SYNTHESIS OF HEXAMETHYLENEAMIDES OF ORGANIC ACIDS

G. S. Kolesnikov, T. V. Smirnova, L. I. Mizrakh,
N. N. Mikhailovskaya and L. I. Shcherbo

In continuation of work on synthesis of derivatives of hexamethyleneimine [1], we attempted to prepare and characterize the hexamethyleneamides of organic acids of various types. The hexamethyleneamide of formic acid is described as a solvent for polyacrylonitrile in the patent literature [2]. This is the only reference to hexamethyleneamides of organic acids in the literature.

The hexamethyleneamide of formic acid is obtained by the action of hexamethyleneimine on formic acid and subsequent dehydration of the salt of hexamethyleneimine with formic acid.

$$(CH_2)_6NH + HCOOH \longrightarrow (CH_2)_6NH \cdot HCOOH$$
$$(CH_2)_6NH \cdot HCOOH \longrightarrow (CH_2)_6NCOH + H_2O$$

The hexamethyleneamide of acetic acid is synthesized by reaction of excess of hexamethyleneimine with acetyl chloride.

$$2(CH_2)_6NH + CH_3COCl \longrightarrow (CH_2)_6NCOCH_3 + (CH_2)_6NH \cdot HCl$$

In similar fashion are prepared the hexamethyleneamides of benzoic, carbonic, fluoroacetic, chloroacetic, bromoacetic, iodoacetic and β-bromopropionic acids. The hexamethyleneamides of methacrylic acid and benzenesulfonic acid are obtained by reaction of the acid chlorides of these acids with hexamethyleneimine in presence of pyridine.

$$(CH_2)_6NH + CH_2{=}C(CH_3)COCl \xrightarrow{C_5H_5N} (CH_2)_6NCOC(CH_3){=}CH_2$$
$$(CH_2)_6NH + C_6H_5SO_2Cl \xrightarrow{C_5H_5N} (CH_2)_6NSO_2C_6H_5$$

The hexamethyleneamide of hexamethyleneaminoacetic acid is prepared by reaction of chloroacetyl chloride with excess of hexamethyleneimine with heating.

$$ClCH_2COCl + 4(CH_2)_6NH \longrightarrow (CH_2)_6NCH_2CON(CH_2)_6 + 2(CH_2)_6NH \cdot HCl$$

Results are presented in the table.

EXPERIMENTAL

Hexamethyleneamide of formic acid (I). Formic acid was gradually run into 25 g of hexamethyleneimine until the liquid was acid to congo. The fraction with b. p. up to 112° was taken off at normal pressure, after which the distillation was continued in vacuo to give 17.4 g of (I) with b. p. 127-130° (23 mm); yield 56%.

Found: M 128.7, 127.9. $C_7H_{13}ON$. Calculated: M 127.2.

Hexamethyleneamide of acetic acid (II). 100 g of hexamethyleneimine and 100 ml of benzene were placed in a flask fitted with stirrer, reflux condenser, dropping funnel and thermometer; dropwise addition was then made, while stirring and cooling with ice (flask temperature 10-15°), of 40 g of acetyl chloride. Hexamethyleneimine hydrochloride was filtered off and washed with benzene. (II) was isolated from the filtrate after the

Hexamethyleneamides of Organic Acids

Hexamethyleneamide of (acid)	Yield (%)	Boiling point	Residual pressure	d_{20}^{20}	n_D^{20}
Formic	56.0	127—130°	23	1.022	1.4903
Acetic	33.5	113—115	8	1.0069	1.489
Fluoroacetic	20.2	102—105	1—2	1.0800 (d_{25}^{25})	1.4832 *
Chloroacetic	33.0	122—124	4	1.1802	1.5152
Bromoacetic	18.4	144—146	6—7	1.5241	1.5430
Iodoacetic	22.0	111—112	4	—	—
Methacrylic	61.0	97—100	2	0.9933	1.4956
Carbonic	30.3	159—160	5	1.053	1.5161 *
β-Bromopropionic	15.0	111—112	1—2	—	1.5112
Benzoic	40.0	147; m.p. 31°	1—2	—	
Benzenesulfonic	58.5	195—197; m.p. 27—28°	2	—	—
Hexamethyleneaminoacetic	35.0	178—180	5	1.0201	1.5094

* At 25° (n_D^{25}).

benzene had been distilled off. After two distillations in vacuo the product had b. p. 113-115° (8 mm); yield 23 g (33.5%).

Found: M 140.2, 138.5. $C_8H_{15}ON$. Calculated: M 141.3.

Hexamethyleneamide of fluoroacetic acid (III). Sodium fluoroacetate. A few drops of phenolphthalein were added to 53 g of ethyl fluoroacetate in a flask provided with stirrer, reflux condenser and dropping funnel; this was followed by addition of 30-40% sodium hydroxide solution in 2-3 ml portions until a permanent coloration appeared; the color was then removed by addition of a few drops of ethyl fluoroacetate. The solution was concentrated until cloudy and the sodium fluoroacetate was precipitated by addition of 500 ml of alcohol-acetone mixture (1:4); the yield of air-dry material was 42 g (92.4%).

Fluoroacetyl chloride. 20 g of sodium fluoroacetate was put into a three-necked flask fitted with stirrer, reflux condenser and dropping funnel, and 20 ml of phosphorus oxychloride was run in. The mixture was heated to 110-120° in the course of 15 minutes, after which the fluoroacetyl chloride was distilled off at 70-80°. Redistillation gave a 71-73° fraction; yield 12 g (61.2%).

According to the literature, fluoroacetyl chloride boils at 72.5° [3].

Hexamethyleneamide of fluoroacetic acid (III). This amide was synthesized in the same manner as (II), from 13 g of fluoroacetyl chloride and 26.7 g of hexamethyleneimine in 75 ml of acetone, except that the hexamethyleneimine was added to the acid chloride solution in acetone at a temperature not exceeding 25-30°. Removal of the acetone left 4.3 g of (III) with b.p. 102-105° (1-2 mm); yield 20.2%.

Found %: N 8.46, 8.62. $C_8H_{14}ONF$. Calculated %: N 8.79.

Hexamethyleneamide of chloroacetic acid (IV). Synthesized in the same way as (II), starting from 23 g of chloroacetyl chloride and 40 g of hexamethyleneimine in 100 ml of benzene (or acetone); yield 12.7 g (33%) of (IV) with b.p. 122-124° (4 mm).

Found %: N 7.60, 7.88. $C_8H_{14}ONCl$. Calculated %: N 8.65.

Hexamethyleneamide of bromoacetic acid (V). Procedure as for (III). 40.4 g of bromoacetyl bromide and 39.2 g of hexamethyleneimine in 75 ml of acetone gave 8 g of (V) with b. p. 144-146° (6-7 mm); yield 18.4%.

Found %: N 6.00, 6.44. $C_8H_{14}ONBr$. Calculated %: N 6.36.

Hexamethyleneamide of iodoacetic acid (VI). Same procedure as for (III). 40.8 g of iodoacetyl chloride and 40 g of hexamethyleneimine in 75 ml of acetone gave 11.7 of (VI) with b. p. 111-112° (4 mm); yield 22%.

Found %: N 5.00, 4.70. $C_8H_{14}ONI$. Calculated %: N 5.24.

Hexamethyleneamide of methacrylic acid (VII). 119 g of pyridine and 49.5 g of hexamethyleneimine were placed in a three-necked flask fitted with stirrer, reflux condenser, dropping funnel and thermometer, and addition was made in the course of 3 hours of 52.3 g of methacrylyl chloride while maintaining the temperature inside the flask at 10-15°. The reaction mixture was run into 500 ml of 10% hydrochloric acid, the organic layer was separated, and the aqueous layer was extracted with benzene 6 times (each time with 50 ml). The benzene extracts were combined with the organic layer and the whole washed with 100 ml of 10% hydrochloric acid and 4-5 times with water; the benzene was distilled off and the residue distilled in vacuo to give 51 g of (VII) with b.p. 97-100° (2 mm); yield 61%.

Found: M 169.5, 168.3. $C_{10}H_7ON$. Calculated: M 167.2.

Hexamethyleneamide of carbonic acid (VIII). 87.5 g of hexamethyleneimine and 300 ml of benzene were placed in a flask fitted with reflux condenser, stirrer, thermometer and bubbler; phosgene was passed through while the temperature was raised to 38-40° in the flask; the completion of the reaction was indicated by fall of temperature in the flask and disappearance of the white opalescence over the surface of the liquid in the flask. Dissolved phosgene was removed by heating the reaction mixture on a boiling water bath for 20-30 minutes. The mixture was then cooled and filtered; the benzene was distilled off from the filtrate, and the residue was distilled in vacuo to give 15 g of (VIII) with b. p. 159-160° (5 mm); yield 30.3%

Found %: N 12.64, 12.25. M 234.0, 231.1. $C_{13}H_{24}ON_2$. Calculated %: N 12.49. M 224.3.

Hexamethyleneamide of β-bromopropionic acid (IX). β-Bromopropionic acid (X). 0.5 g of hydroquinone and 10 g of acrylic acid were placed in a flask fitted with reflux condenser, dropping funnel and bubbler; passage of a stream of dry hydrogen bromide was started simultaneously with dropwise introduction of acrylic acid; a total of 40 g of acrylic acid was taken. Hydrogen bromide was passed in until the contents of the flask had completely solidified. Yield of (X) 78 g (92%). M. p. 59.5-61°; the literature gives 62° [4].

β-Bromopropionyl chloride (XI). 30 g of (X) was placed in a flask fitted with stirrer, reflux condenser and dropping funnel; the flask was heated to 80-85°, and 24 g of thionyl chloride gradually stirred in. Heating was continued until hydrogen chloride ceased to come off; distillation gave 14.3 g of (XI) with b.p. 155-158°; yield 42%.

Found %: Cl 20.60, 20.52. C_3H_4OClBr. Calculated %: Cl 20.69.

Hexamethyleneamide of β-bromopropionic acid (IX) was obtained in the same manner as (III). 10 g of (XI) and 12 g of hexamethyleneimine in 50 ml of acetone gave 2.2 g of (IX) with b.p. 111-112° (1-2 mm); yield 15%.

Found %: N 5.38, 5.85. $C_9H_{16}ONBr$. Calculated %: N 5.98.

Hexamethyleneamide of benzoic acid (XII) was obtained in the same manner as (II). 90 g of hexamethyleneimine and 70 g of benzoyl chloride in 150 ml of benzene gave 40.2 g of (XII) with b.p. 147° (1-2 mm), m.p. 31°; yield 40%.

Found %: N 6.91, 6.69. M 196.5, 198.7. $C_{13}H_{17}ON$. Calculated %: N 6.89. M 203.1.

Hexamethyleneamide of benzenesulfonic acid (XIII) was obtained in the same manner as (VII). 49.5 g of hexamethyleneimine and 88.3 g of benzenesulfonyl chloride in presence of 119 g of pyridine gave 70 g of (XIII) with b.p. 195-197° (2 mm); yield 58.5%. Recrystallization from methyl alcohol yielded colorless crystals with m. p. 27-28°.

Found %: N 5.81, 6.11. $C_{12}H_{17}O_2NS$. Calculated %: N 5.86.

Hexamethyleneamide of hexamethyleneaminoacetic acid (XIV). 30 g of chloroacetyl chloride and 120 ml of benzene were placed in a flask fitted with stirrer, reflux condenser and dropping funnel, and 105 g of hexamethyleneimine were added in the course of 15 minutes with stirring and external cooling. The mass was then heated for 3 hours at 80-90°, cooled and filtered. The benzene was distilled off from the filtrate and the residue distilled in vacuo to give 25 g of (XIV) with b. p. 178-180° (5 mm); yield 35%.

Found %: N 11.74, 11.70. $C_{14}H_{26}ON_2$. Calculated %: N 11.75.

SUMMARY

12 hexamethyleneamides of organic acids were synthesized; 11 of these are described for the first time.

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CARBOCHAIN POLYMERS AND COPOLYMERS

II. SYNTHESIS AND POLYMERIZATION OF 2-ALKOXYSTYRENES

G. S. Kolesnikov and G. M. Pogosyan

We have described the synthesis and polymerization of 4-alkoxystyrenes and have shown that the introduction of an oxygen atom between the aromatic ring and the aliphatic radical of the substituent leads to a higher temperature of vitrification in the n-alkoxystyrene series. With the objective of clarifying the influence of the position of the substituent on the vitrification temperature of polymers of alkoxystyrenes, we undertook the synthesis and polymerization of 2-alkoxystyrenes. The monomers were synthesized in similar fashion to 4-alkoxystyrenes, starting from 2-bromophenol which was converted into 2-alkoxybromobenzenes. Polymerization of 2-alkoxystyrenes gave polymers whose vitrification temperature was determined after reprecipitation. Results are presented in the table.

2-Alkoxystyrenes

Alkoxy group	Yield in %	Boiling point	Residual pressure (mm)	d_4^{20}	n_D^{20}	Vitrification temperature of polymer
2-Methoxy-	55.8	82—84°	12	1.0100	1.5620	86°
2-Ethoxy-	60.8	112—113	27	0.9914	1.5468	83
2-n-Propoxy-	61.1	105—107	13—14	0.9803	1.5344	73
2-n-Butoxy-	53.7	120—122	13	0.9551	1.5318	46
2-Isoamyloxy-	43.2	126—129	14	0.9506	1.5250	57
2-n-Nonyloxy-	50.0	175—177	13	0.9296	1.5104	6

The table indicates that in the n-alkoxystyrene series the vitrification temperature of the polymers falls with increasing length of radical entering into the composition of the alkoxy group, just as was observed in the case of polymers of 4-alkoxystyrenes and 4-alkylstyrenes [1]. The vitrification temperature of polymers of 2-alkoxystyrenes is somewhat below the temperature of vitrification of polymers of 4-alkoxystyrenes, possibly due in our opinion to steric hindrance created by the alkoxy groups located in the ortho-position to the main chain of the polymer so that the polymeric molecules would be more loosely packed.

The vitrification temperatures of polymers of 2-alkoxystyrenes were determined by B. L. Tsetlin to whom we express our deep thanks.

EXPERIMENTAL

2-Methoxybromobenzene (I) was obtained in the same fashion as 4-methoxybromobenzene. 173 g of 2-bromobenzene, 56 g of potassium hydroxide and 170.4 g of methyl iodided in 200 ml of alcohol gave 140 g of (I) with b. p. 94-96° (10 mm); yield 74.8%.

β-(2-Methoxyphenyl)-ethyl alcohol (II) was obtained in the same manner as β-(4-methoxyphenyl)-ethyl alcohol. From 187 g of (I), 24 g of magnesium and 52 g of ethylene oxide in 600 ml of absolute ether (total

volume) was obtained 63.4 g of (II) with b. p. 134-136° (14 mm); yield 41.7%.

2-Methoxystyrene (III) was prepared by dehydration of 38 g of (II) with the help of 18.2 g of potassium hydroxide in presence of 1 g of hydroquinone; the yield of (III) with b.p. 82-84° (12 mm) was 18.7 g (55.8%).

2-Ethoxybromobenzene (IV) was prepared in the same manner as (I). From 173 g of 2-bromophenol, 56 g of potassium hydroxide and 130.8 g of ethyl bromide in 200 ml of alcohol was obtained 177 g of (IV) with b.p. 221-224°; yield 88%.

β-(2-Ethoxyphenyl)-ethyl alcohol (V) was obtained in the same manner as (II). From 172 g of (IV), 20 g of magnesium and 40 g of ethylene oxide was obtained 83 g of (V) with b. p. 141-145° (16-17 mm); yield 58%.

Found %: C 72.07, 71.85; H 8.32, 8.34. $C_{10}H_{14}O_2$. Calculated %: C 72.25; H 8.49.

2-Ethoxystyrene (VI) was prepared by dehydration of 83 g of (V) with the help of 37 g of potassium hydroxide in presence of 2 g of hydroquinone; yield of (VI) with b. p. 112-113° (27 mm) or 94-96° (13 mm) 45 g (60.8%).

2-n-Propoxybromobenzene (VII) was obtained in the same manner as (I). From 173 g of 2-bromophenol, 56 g of potassium hydroxide and 135.3 g of n-propyl bromide in 200 ml of alcohol was obtained 151 g of (VII) with b. p. 116-118° (13-14 mm); yield 70.2%.

β-(2-n-Propoxyphenyl)-ethyl alcohol (VIII) was obtained in the same manner as (II). 150 g of (VII), 16 g of magnesium and 30 g of ethylene oxide gave 89 g of (VIII) with b.p. 149-154° (16 mm); yield 71%.

2-n-Propoxystyrene (IX) was obtained by dehydration of 89 g of (VIII) with the help of 36 g of potassium hydroxide in presence of 2 g of hydroquinone; b. p. 126-128° (30 mm) or 105-107° (13-14 mm); yield 49 g (61.1%).

2-n-Butoxybromobenzene (X) was obtained in the same manner as (I). From 173 g of 2-bromophenol, 56 g of potassium hydroxide and 150.7 g of n-butyl bromide in 200 ml of alcohol was obtained 164 g of (X) with b. p. 248-250° or 134-135° (16 mm); yield 71.6%.

Found %: C 52.56, 52.54; H 5.76, 5.78; Br 34.64; 34.68. $C_{10}H_{13}OBr$. Calculated %: C 52.44; H 5.71; Br 34.90.

β-(2-n-Butoxyphenyl)-ethyl alcohol (XI) was obtained in the same manner as (II). From 160 g of (X), 16.8 g of magnesium and 32 g of ethylene oxide was obtained 82 g of (XI) with b. p. 150-154° (12 mm); yield 60.5%.

2-n-Butoxystyrene (XII) was obtained by dehydration of 82 g of (XI) with the help of 31 g of potassium hydroxide in presence of 2 g of hydroquinone; b. p. 155-157° (56 mm) or 120-122° (13 mm); yield 40 g (53.7%).

2-Isoamyloxybromobenzene (XIII) was obtained in the same manner as (I). 173 g of 2-bromophenol, 56 g of potassium hydroxide and 151 g of isoamyl bromide in 200 ml of alcohol gave 164 g of (XIII) with b. p. 142-143° (16 mm); yield 64.9%.

Found %: C 54.46, 54.46; H 6.23, 6.22; Br 33.16, 33.16. $C_{11}H_{15}OBr$. Calculated %: C 54.32; H 6.21; Br 32.89.

β-(2-Isoamyloxyphenyl)-ethyl alcohol (XIV) was prepared in the same manner as (II). 160 g of (XIII), 15.8 g of magnesium and 31 g of ethylene oxide gave 86 g of (XIV) with b. p. 155-159° (11 mm); yield 62.7%.

2-Isoamyloxystyrene (XV) was prepared by dehydration of 86 g of (XIV) with the help of 30 g of potassium hydroxide in presence of 2 g of hydroquinone; b. p. of (XV) 126-129° (14 mm); yield 33.9 g (43.2%).

n-Nonyl bromide (XVI). 270 ml of water, 308 g of sodium bromide and 345.6 g of n-nonyl alcohol were put into a round-bottomed flask (1-liter capacity) fitted with reflux condenser, stirrer and dropping funnel; dropwise addition with stirring was made of 400 g of conc. sulfuric acid, after which the reaction mixture was boiled for 6-8 hours. The organic layer was separated, washed with water and 5% sodium carbonate solution, dried with calcium chloride, and distilled in vacuo; the fraction with b.p. 94-97° (13-14 mm) was collected; yield of (XVI) 272 g (54.9%).

2-n-Nonyloxybromobenzene (XVII) was synthesized in the same manner as (I). From 113.6 g of 2-bromophenol, 36.7 g of potassium hydroxide and 136 g of (XVI) in 135 ml of alcohol was obtained 144 g of (XVII) with b. p. 179-181° (7-8 mm) or 183-185° (10 mm); yield 76%.

Found %: C 60.05, 60.23; H 7.80, 7.74; Br 26.48, 26.51; $C_{15}H_{23}OBr$. Calculated %: C 60.18; H 7.74; Br 26.72.

β-(2-n-Nonyloxyphenyl)-ethyl alcohol (XVIII) was obtained in the same manner as (II). 140 g of (XVI), 11 g of magnesium and 25 g of ethylene oxide gave 64 g of (XVIII) with b.p. 200-203° (10 mm); yield 51.6%.

2-n-Nonyloxystyrene (XIX) was prepared by dehydration of 18.2 g of (XVIII) with the help of 5 g of potassium hydroxide in presence of 0.5 g of hydroquinone; yield of (XIX) 8.5 g (50%); b. p. 175-177° (13 mm).

SUMMARY

Six 2-alkoxystyrenes were synthesized, five of them for the first time; their polymers were prepared and the vitrification temperatures of the latter were determined.

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INVESTIGATIONS IN THE NAPHTHALENE SERIES

XVII.* THE PHOTOSENSITIVITY OF AROMATIC SELENIUM-CONTAINING COMPOUNDS. 1-NITRONAPHTHALENE-5-, 1-NITRONAPHTHALENE-2- AND 1-NITRONAPHTHALENE-4-SELENIOUS ACIDS

V. V. Kozlov

In continuation of the study of the photosensitivity of selenium-containing compounds of nitronaphthalene [1], we have synthesized other isomeric nitronaphthalene-selenious acids. We effected their preparation by the general scheme of transformation of diazotized isomeric nitronaphthylamines.

$$C_{10}H_6NO_2NH_2 \xrightarrow{CH_3COOH+NaNO_2} C_{10}H_6NO_2N_2OOCCH_3 \xrightarrow{KS\cdot CN} \longrightarrow C_{10}H_6NO_2N_2SeCN \xrightarrow{O_2} C_{10}H_6NO_2SeO_2H$$

Diazotization of nitronaphthylamines is most conveniently conducted in acetic acid solution with dry nitrite. Oxidation of the nitroselenocyanonaphthalene is advantageously effected by boiling with 20% nitric acid.

Aqueous solutions of isomeric nitronaphthalene selenious acids and wool cloth impregnated with such solutions vary in their behavior in sunlight. Thus, the 1,5-nitroselenious acid and its salts do not change color; exposure to light brings about a slight change in color of wool cloth impregnated with an aqueous or alcoholic solution of the 1,2-nitroselenious acid on drying; under similar conditions, cloth impregnated with solutions of the 1,4-nitroselenious acid undergo marked color change on exposure – from yellow (before insolation) to brown (after insolation). The values of photosensitivity of the isomeric nitronaphthalene selenious acids in comparison with their sulfur-containing analogs are given in the table.

Substance	Degrees of photosensitivity
1-Nitronaphthalene-2-sulfinic acid [2]	0.11
1-Nitronaphthalene-2-selenious acid	0.10
1-Nitronaphthalene-4-sulfinic acid [2]	Not photosensitive
1-Nitronaphthalene-4-selenious acid	0.4
1-Nitronaphthalene-5-sulfinic acid [3]	Not photosensitive
1-Nitronaphthalene-5-selenious acid	Not photosensitive
1-Nitronaphthalene-8-sulfinic acid [3]	0.5
1-Nitronaphthalene-8-selenious acid [1]	1.0

* Previous communication in J. Gen. Chem., 27, 1156 (1957), (See C. B. translation).

EXPERIMENTAL

Preparation of 1,5-nitroselenocyanonaphthalene (I). 17 g of 1-nitro-5-naphthylamine (m.p. 115°) was dissolved in 300 ml of glacial acetic acid and diazotized at 5-8° with 10 g of dry nitrite. The filtered solution was slowly run with stirring into a solution of 40 g of KSeCN in 50 ml of water. After keeping for 2 hours, the reaction mass was poured into 2 liters of water. The precipitate was filtered, washed with water, then with hot alcohol, and dried in a desiccator. Yield of crude product 23 g (92%). The product is insoluble in water, and soluble in conc. sulfuric acid with a blue-violet color. It crystallizes from dilute acetic acid; m.p. 76° (with decomp.).

Oxidation of (I). This was effected on the same lines as oxidation of 1,8-nitroselenocyanonaphthalene [1] by boiling with 20% nitric acid. Yield of 1-nitronaphthalene-5-selenious acid (II) 80%. The substance is sparingly soluble in alcohol, and soluble in sodium carbonate. It crystallizes from water in the form of fine needles with m.p. 145°. It partly resinifies on prolonged heating with water. It is more soluble in water than the 1,8-isomer.

Found %: H_2O 6.01. $C_{10}H_6(NO_2)SeO_2H \cdot H_2O$. Calculated %: H_2O 5.96. Found %: C 42.38; H 2.58; N 5.02; Se 26.98. $C_{10}H_7O_4NSe$. Calculated %: C 42.2; H 2.45; N 4.92; Se 27.8.

Salts with metals. Preliminary experiments in which a 0.1 N solution of the ammonium salt of the 1-nitro-5-selenious acid (III) was mixed with 0.1 N solutions of inorganic salts containing various cations established that the most difficultly soluble are the lead, copper, silver, zinc, ferrous and calcium salts. The aluminum, magnesium, barium, sodium and potassium salts have better solubility. The ammonium and ferric salts possess the highest solubility.

Copper salt $(C_{10}H_6NO_2SeO_2)_2Cu \cdot H_2O$ was obtained in the form of dark-brown granules by reacting a solution of (III) with copper sulfate. The salt is insoluble in water and crystallizes from 80% alcohol.

Found %: H_2O 2.72. $C_{20}H_{12}O_8N_2Se_2Cu \cdot H_2O$. Calculated %: H_2O 2.78. Found %: Cu 10.83. $C_{20}H_{12}O_8N_2Se_2Cu$. Calculated %: Cu 10.12.

The ferrous salt $(C_{10}H_6NO_2SeO_2)_2Fe \cdot 2.5\ H_2O$ was prepared by reacting a solution of (III) with ferrous sulfate. The salt is insoluble in water and crystallizes from 80% alcohol in the form of greenish-brown granules.

Found %: H_2O 6.27. $C_{20}H_{12}O_8N_2Se_2Fe \cdot 2.5\ H_2O$. Calculated %: H_2O 6.73.
Found %: Fe 9.47. $C_{20}H_{12}O_8N_2Se_2Fe$. Calculated %: Fe 8.97.

The lead salt $(C_{10}H_6NO_2SeO_2)_2Pb \cdot 2H_2O$ was obtained by reacting a solution of (III) with lead nitrate. The salt is insoluble in water and crystallizes from 50% alcohol.

Found %: H_2O 4.79. $C_{20}H_{12}O_8N_2Se_2Pb \cdot 2H_2O$. Calculated %: H_2O 4.48.
Found %: Pb 27.14. $C_{20}H_{12}O_8N_2Se_2Pb$. Calculated %: Pb 26.81.

The calcium salt $(C_{10}H_6NO_2SeO_2)_2Ca \cdot H_2O$ was prepared by reacting a solution of (III) with calcium chloride. The salt is insoluble in water and crystallizes from 50% alcohol in the form of dark-yellow plates.

Found %: H_2O 2.91. $C_{20}H_{12}O_8N_2Se_2Ca \cdot H_2O$. Calculated %: H_2O 2.87. Found %: Ca 6.64. $C_{20}H_{12}O_8N_2Se_2Ca$. Calculated %: Ca 6.57.

The aluminum salt $(C_{10}H_6NO_2SeO_2)_3Al \cdot 3H_2O$ was obtained by reacting (III) with aluminum sulfate. The salt crystallizes from 20% alcohol in the form of yellow plates.

Found %: H_2O 5.94. $C_{30}H_{18}O_{12}N_3Se_3Al \cdot 3H_2O$. Calculated %: H_2O 5.8. Found %: Al 4.68. $C_{30}H_{18}O_{12}N_3Se_3Al$. Calculated %: Al 4.51.

The zinc salt $(C_{10}H_6NO_2SeO_2)_2Zn \cdot H_2O$ was prepared by reacting a solution of (III) with zinc sulfate. The salt is insoluble in water and crystallizes from 80% alcohol in the form of yellow-brown plates.

Found %: H_2O 2.82. $C_{20}H_{12}O_8N_2Se_2Zn \cdot H_2O$. Calculated %: H_2O 2.78. Found %: Zn 10.31. $C_{20}H_{12}O_8N_2Se_2Zn$. Calculated %: Zn 10.26.

The silver salt $C_{10}H_6NO_2SeO_2Ag \cdot H_2O$ was obtained by reacting a solution of (III) with silver nitrate. The salt is insoluble in water and crystallizes from 50% alcohol in the form of brown plates.

Found %: H_2O 4.52. $C_{10}H_6O_4NSeAg \cdot H_2O$. Calculated %: H_2O 4.4.
Found %: Ag 27.31. $C_{10}H_6O_4NSeAg$. Calculated %: Ag 27.5.

The ferric salt $(C_{10}H_6NO_2SeO_2)_3Fe \cdot 5H_2O$ was obtained by reacting a solution of (III) with ferric chloride. The salt has good solubility in water and crystallizes from 25% alcohol in the form of yellow-brown prisms.

Found %: H_2O 9.28. $C_{30}H_{18}O_{12}N_3Se_3Fe \cdot 5H_2O$. Calculated %: H_2O 9.14.
Found %: Fe 5.86. $C_{30}H_{18}O_{12}N_3Se_3Fe$. Calculated %: Fe 5.71.

The barium salt $(C_{10}H_6NO_2SeO_2)_2Ba \cdot 2H_2O$ was obtained by reacting a solution of (III) with barium chloride. The salt is sparingly soluble in water and crystallizes from 80% acetic acid in the form of light-brown granules.

Found %: H_2O 5.02. $C_{20}H_{12}O_8N_2Se_2Ba \cdot 2H_2O$. Calculated %: H_2O 4.87. Found %: Ba 19.60.
$C_{20}H_{12}O_8N_2Se_2Ba$. Calculated %: Ba 19.48.

The magnesium salt $(C_{10}H_6NO_2SeO_2)_2Mg \cdot 4H_2O$ was prepared by reaction of a solution of (III) with magnesium chloride. The salt crystallizes from dilute alcohol in the form of light-brown granules.

Found %: H_2O 11.02. $C_{20}H_{12}O_8N_2Se_2Mg \cdot 4H_2O$. Calculated %: H_2O 10.87. Found %: Mg 4.22.
$C_{20}H_{12}O_8N_2Se_2Mg$. Calculated %: Mg 4.06.

Salts with amines. Treatment of 0.4 N solution of (III) with one equivalent of the hydrochloride of an aromatic amine gives in a number of cases a precipitate of amine salt and nitronaphthalene selenious acid. The salt with aniline is readily soluble in water. Salts with the following bases are soluble in hot water: p-anisidine (brown plates), p-toluidine (brown granules), o-anisidine (yellow needles), and dianisidine (red-brown rods). α-Naphthylamine gives brown plates, soluble on heating. With an excess of α-naphthylamine hydrochloride, the precipitate is lighter in color, is insoluble in water, and resinifies on heating. The salt with β-naphthylamine is in the form of colorless plates which crystallize from dilute alcohol; m.p. 87°. The salt with benzidine consists of long light-yellow needles with m.p. 135°; the filtrate has a blue-violet color. When heated under liquid, the salt at first turns green and then black.

Preparation of 1,2-nitroselenocyanonaphthalene (IV). Starting from 1-nitro-2-naphthylamine (m.p. 186°), the same procedure as for (I) was followed. Yield of crude product 95%. Soluble in alcohol and ammonia, insoluble in water, difficultly soluble in concentrated sulfuric acid. Crystallizes from acetic anhydride in the form of golden needles with m.p. 156°.

(IV) was oxidized in the same manner as for the preparation of (II). 1-Nitronaphthalene-2-selenious acid is soluble in alcohol, acetic acid and pyridine. Very sparingly soluble in water, easily soluble in ammonia and sodium carbonate solution. Fine crystals, m. p. 194°.

Found %: C 42.1; H 2.62; N 4.98; Se 27.22. $C_{10}H_7O_4NSe$. Calculated %: C 42.2; H 2.45; N 4.92; Se 27.81.

Preparation of 1,4-nitroselenocyanonaphthalene (V). Prepared from 1-nitro-4-naphthylamine (m.p. 194°) in the same way as (I). Yield of crude product 70%. Insoluble in pyridine, chloroform and benzene, slightly soluble in alcohol. Crystallizes from acetic acid as yellow crystals. Heating with conc. ammonia converts the substance into 1-nitro-4-naphthylamine as a consequence of replacement of the SeCN group by the amino group.

Preparation and properties of 1-nitronaphthalene-4-selenious acid. Oxidation of (V) was performed on the same lines as in the synthesis of (II). The product separates as the sodium salt which crystallizes from water as bright-yellow needles. On heating with sodium sulfite, a solution of this substance in water, likewise the mother liquor after separation of the crude product, deposits a crimson precipitate which is dinitrodinaphthyl diselenide.

Found %: H_2O 14.67. $C_{10}H_6NO_2SeO_2Na \cdot 3H_2O$. Calculated %: H_2O 15.0.
Found %: C 39.08; H 2.02; N 4.67; Se 25.54; Na 7.71. $C_{10}H_6O_4NSeNa$. Calculated %: C 39.21; H 1.96; N 4.67; Se 25.98; Na 7.51.

SUMMARY

1. Isomeric nitronaphthalene selenious acids (1,2; 1,4; 1,5) and their salts were prepared.

2. It was established that 1,5-nitronaphthalene selenious acid is not photosensitive; the 1,2-nitroselenious

acid is weakly photosensitive, in full accord with the reaction to light of the isomeric sulfur-containing analogs (nitronaphthalenesulfinic acids).

3. It was established that 1-nitronaphthalene-4-selenious acid has appreciable photosensitivity in contrast to its sulfur-containing analog (1-nitronaphthalene-4-sulfinic acid).

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INVESTIGATION OF THE PRODUCTS OF CONDENSATION OF HENDECENOIC ACID WITH FORMALDEHYDE

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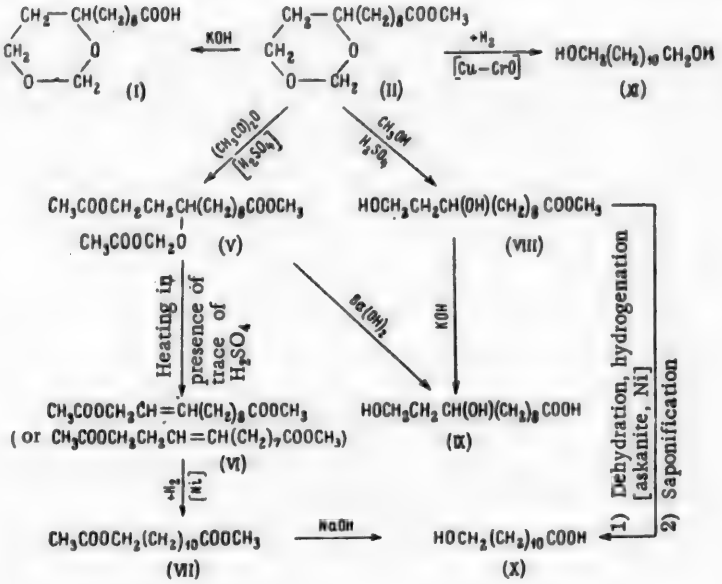
In the search for a convenient method of preparation of 12-hydroxylauric acid we realized the condensation of hendecenoic acid with formaldehyde (Prins reaction) and studied some of the transformations of the compounds formed in this reaction. A similar condensation of formaldehyde with unsaturated acids has previously only been described in two papers [1, 2]; only one of these [1] contains data relating to hendecenoic acid. Transformations of products of condensation of hendecenoic acid with formaldehyde have not, however, previously been investigated.

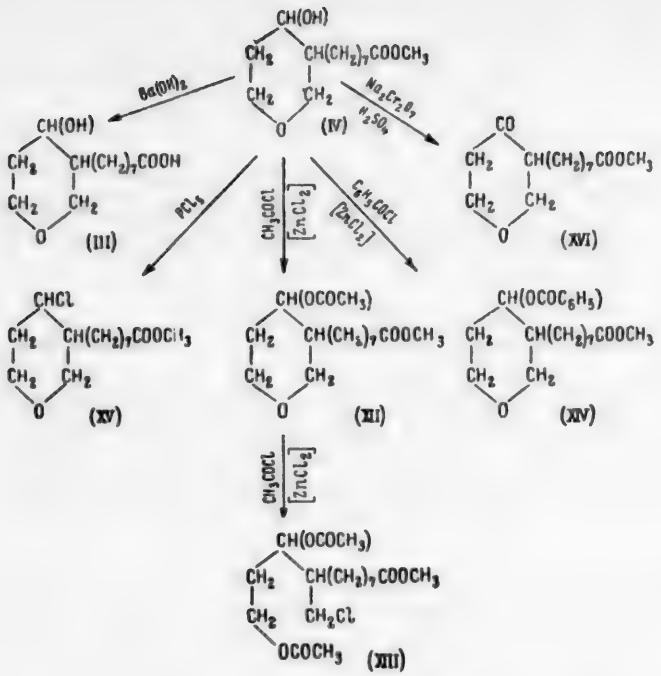
We performed the condensation by heating hendecenoic acid with formaldehyde (38-42%) in presence of sulfuric acid (10-12% of the weight of the reaction mixture) for 6 hours at 80-85°. Formation of the following substances in this reaction was established: 4-(ω-carboxyoctyl)-1,3-dioxan (I, yield about 30%).•• 4-(ω-carbomethoxyoctyl)-1,3-dioxan (II, yield about 17%). 3-(ω-carboxymethoxyheptyl)-4-hydroxytetrahydropyran (IV, yield about 1%), and a small quantity of 10-hydroxyhendecanoic acid. It should be noted that acids (I) and (III) are present in the reaction mixture partly in the form of their methyl esters, whose formation we observed not only when using formalin (which could contain methyl alcohol) but also when working with paraformaldehyde.

The structure of compounds (II) and (IV) was confirmed by a series of transformations as represented by the following schemes.



• Part of the Candidate's Dissertation of N.P. Solovyeva.

•• It was convenient not to isolate this acid (the same applies to acid (III) from the reaction mixture as such, but to convert it to the methyl ester which is easily isolated by fractionation in vacuo.



These transformations also showed that (II) may be transformed into 12-hydroxylauric acid (X); the yield of (X), however, was only 30% of the theoretical, calculated on the (II).

EXPERIMENTAL

1. Condensation of Hendecenoic Acid With Formaldehyde

100 g of sulfuric acid (d 1.84) was added to a mixture of 500 g of formaldehyde solution (38-40%) and 250 g of hendecenoic acid (m.p. 21-22.5°), and the mass stirred for 6 hours at 90-95°. The upper layer was then separated, diluted with ether, and washed with salt solution until neutral. After removal of the solvent, the residue was treated with aqueous alcoholic (1 : 1) solution of potassium hydroxide (10%) and the neutral products were extracted with ether. From the ethereal extract was separated 36.5 g of a mixture of neutral substances; acidification of the alkaline solution led to separation of 255 g of a mixture of acidic substances.

Investigation of the neutral portion. Fractional distillation in vacuo gave the following products.

Methyl hendecenoate, 1.7 g.

B. p. 98-100° at 2 mm, d_4^{20} 0.882, n_D^{20} 1.4400, MR_D 59.25; calc. 58.90. Literature data: b. p. 98° at 2 mm [3], d_4^{20} 0.889, n_D^{20} 1.4398 [4].

Found %: C 72.53, 72.51; H 11.19, 11.40; ester number (e.n.) 284.3; bromine number 78.0. $C_{12}H_{22}O_2$. Calculated %: C 72.71; H 11.17; e.n. 282.1; bromine number 80.8.

Methyl 10-hydroxyhendecanoate. The fraction with b.p. 127-130° at 2 mm contains methyl 10-hydroxyundecanoate in admixture with the ester of hendecenoic acid.

Found %: OH 3.37 (by acetylation); e.n. 270.25; bromine number 26.8. $C_{12}H_{24}O_3$. Calculated %: OH 7.8; e.n. 258.5.

The presence of the ester of 10-hydroxyhendecanoic acid in this fraction was confirmed by oxidation with chromic acid mixture. From the product of oxidation was isolated a substance with b.p. 130-133° at 4 mm, which on treatment with semicarbazide gave the semicarbazone of methyl 10-ketohendecanoic acid with m.p. 120-121° (from methanol).

Found %: N 15.29. $C_{13}H_{25}O_3N_3$. Calculated %: N 15.49.

4-(ω-Carbomethoxyoctyl)-1,3-dioxan (II) was obtained in a quantity of 9.5 g.

B. p. 155-157° at 3 mm, setting point 29.5-30.4° (long colorless needles).
Found %: C 65.07, 65.02; H 10.20, 10.36; e.n. 216.4. $C_{14}H_{26}O_4$. Calculated %: C 65.08; H 10.15; e.n. 216.8.

Saponification of (II) gave 4-(ω-carboxyoctyl)-1,3-dioxane (I) with m.p. 57.5-58.5° (from 80% alcohol).

Found %: C 63.95, 63.72; H 10.12, 10.13; acid number (a.n.) 229.1. $C_{13}H_{24}O_4$. Calculated %: C 63.90; a.n. 229.2.
Silver salt. Found %: Ag 30.3. $C_{13}H_{23}O_4Ag$. Calculated %: Ag 30.7.

3-(ω-Carbomethoxyheptyl)-4-hydroxytetrahydropyran (IV) was obtained in the amount of 3.5 g.

B.p. 176-178° at 3 mm, d_4^{20} 1.044, n_D^2 1.4698, MR_D^0 69.12, calc. 69.47.
Found %: C 65.33, 65.15; H 10.01, 10.15: e. v. 217.9. $C_{14}H_{26}O_4$. Calculated %: C 65.08; H 10.15; e. v. 216.8.

Saponification of (IV) with barium hydroxide at room temperature gave 3-(ω-carboxyheptyl)-4-hydroxytetrahydropyran (III).

B. p. 192-195° at 4 mm, d_4^{35} 1.060, n_D^{35} 1.4708, MR_D 64.43; calc. 64.85.
Found %: C 64.12, 64.02; H 10.12, 10.31; a.n. 231.1. $C_{13}H_{24}O_4$. Calculated %: C 63.90; H 10.91; a.n. 229.2.

Examination of acidic products. The free acids, isolated from the products of condensation in the amount of 255 g, were esterified at room temperature with 750 ml of anhydrous methanol in presence of gaseous hydrogen chloride (5%). The following products were isolated after appropriate working-up and fractionation in vacuo.

Methyl hendecenoate in quantity of 28.4 g with b.p. 98-101° at 2 mm (the other constants are also close to those given previously).

Methyl 10-hydroxyhendecanoate. In this case also, the acid could not be separated from the accompanying methyl ester of hendecenoic acid. From the product of oxidation with potassium bichromate was obtained the semicarbazone of methyl 10-ketohendecanoate which did not give a depression of melting point in admixture with the product of oxidation of the analogous fraction described above.

4-(ω-Carbomethoxyoctyl)-1,3-dioxan (II) in quantity of 104.3 g.

B.p. 155-156° at 3 mm; setting point 29.5-30° (no depression of setting point in admixture with a specimen isolated from the neutral portion).
Found : C 65.31, 65.09; H 9.90, 10.17; e.n. 218.1. $C_{14}H_{26}O_4$. Calculated %: 65.08; H 10.15; e.n. 216.8.

Hydrolysis of (II) gave acid (I), which did not give a depression of melting point in admixture with the same acid described above.

3-(ω-Carbomethoxyheptyl)-4-hydroxytetrahydropyran (IV) in quantity of 59 g.

B. p. 175-178° at 3 mm, d_4^{20} 1.4698, n_D^{20} 1.043, MR_D 69.10; calc. 69.47.

Found %: C 65.04, 65.09; H 10.25, 10.27; OH 4.7 (by acetylation); bromine number 2.2; e.n. 216.9. $C_{14}H_{26}O_4$. Calculated %: C 65.08; H 10.15; OH 6.64; e.n. 216.8.

Hydrolysis of (IV) gave acid (III), with constants and analytical data characteristic of acid (III) described above.

2 Transformations of 4-(ω-Carbomethoxyoctyl)-1,3-dioxan

Methyl 12-acetoxy-10-acetoxymethoxylaurate (V). 1 g of concentrated sulfuric acid was added to a mixture of 75 g of (I) and 60 g of acetic anhydride, which was then heated on a boiling water bath for 6 hours. 2.5 g of anhydrous sodium acetate was then added and the precipitated sodium sulfate was removed. Distillation in vacuo gave 62 g of (V); yield 58.7%.

B. p. 197-198° at 3 mm, d_4^{20} 1.0484, n_D^{20} 1.4498, MR_D 92.1; calc. 91.92.
Found %: C 59.76, 60.04; H 9.11, 8.97; e.n. 468.3. $C_{18}H_{32}O_7$. Calculated %: C 59.97; H 8.95; e.n. 468.8.

Methyl 12-acetoxy-Δ^{10}-dodecenoate or 12-acetoxy-Δ^9-dodecenoate (VI). Ester (V), prepared by the action of acetic anhydride on (II) (see preceding experiment), was fractionated in vacuo without thorough purification from residues of sulfuric acid (acid reaction to congo). The yield of (VI), which is possibly a mixture of Δ^9- and Δ^{10}-isomers, is 41.3%.

B. p. 151-153° at 3 mm, d_4^{20} 1.0119, n_D^{20} 1.4640, MR_D 73.79; calc. 74.11.
Found %: C 66.43, 66.51; H 9.95, 9.94; e.n. 413.4; bromine number 57.5. $C_{15}H_{26}O_4$. Calculated %: C 66.63; H 9.69; e.n. 414.3; bromine number 59.1.

Methyl 12-acetoxylaurate (VII). 14 g of (VI) was hydrogenated in an autoclave in presence of 1.5 g of Raney nickel at 60-65° and 145 atm. 1.4 liters of hydrogen was absorbed. The catalyst was separated and 13 g of product was obtained; distillation of the latter in vacuo gave 11.3 g of (VII); yield 80%.

B. p. 170-175° at 2 mm, n_D^{20} 1.4499. The literature reports b.p. 150-152° at 0.5 mm [5].
Found: e.n. 409.0. $C_{15}H_{28}O_4$. Calculated: e.n. 411.2.

Methyl 10,12-dihydroxylaurate (VIII). A mixture of 25 g of (II), 0.5 g of sulfuric acid (d 1.84) and 175 ml of methanol in a flask fitted with a dephlegmator was heated in such a manner that methanol and the methylal formed came over at a rate of 8-10 ml per hour. Distillation was continued until a sample of the distilling liquid gave a negative reaction for a carbonyl compound with 2,4-dinitrophenylhydrazine. The product of methanolysis (15 g) was distilled in vacuo and gave 6.1 g of (VIII) or 25.6% yield.

B. p. 165-167° at 3 mm, m.p. 34-34.5°.
Found %: C 63.60, 63.56; H 10.54, 10.39; OH 14.21; e.n. 228.3 (by the Tserevitinov method). $C_{13}H_{26}O_4$. Calculated %: C 63.38; H 10.64; OH 13.8; e.n. 227.3.

10,12-Dihydroxylauric acid (IX). a) 10 g of (V) was mixed with 150 ml of a saturated solution of barium hydroxide and the mixture stood at room temperature for 48 hours. Acidification with hydrochloric acid led to separation of (IX) which was extracted with a 10 : 1 mixture of ether and ethyl acetate. M. p. 86-87° (from benzene).

Found %: C 62.24, 62.25; H 10.20, 10.38; OH 14.32; a.n. 240.1. $C_{12}H_{24}O_4$. Calculated %: C 62.03; H 10.41; OH 14.65; a.n. 241.1.

b) 3 g of (VIII) was heated with 100 ml of 0.5 N alcoholic solution of potassium hydroxide. 1.6 g of (IX) was obtained with m.p. 86-87° (many recrystallizations from benzene). A mixed sample with the acid obtained from (V) did not show a depression of melting point.

12-Hydroxylauric acid (X). a) 15 g of (VII) was heated with 60 ml of 10% aqueous alcoholic (1 : 1) solution of potassium hydroxide. 10.8 g of (X) was obtained or 90% yield.

M.p. 84-85°. Literature: m.p. 84-84.5° [5].
Found %: C 66.67, 66.50; H 11.14, 11.42; OH 7.4 (by acetylation); a.n. 258.7. $C_{12}H_{24}O_3$. Calculated %: C 66.63; H 11.18; OH 7.8; a.n., 259.0.

b) 19 g of (VIII), 2 g of Raney nickel and 0.5 g of Askanite were heated in a hydrogen atmosphere at a pressure of 140 atm and a temperature of 70-120°. The catalyst was separated; the ester of 12-hydroxylauric acid was subjected to acetylation for convenience of collection and purification. For this purpose addition was made to 12 g of the reaction mixture of 50 g of acetic anhydride and 12 g of an acetylating mixture prepared by

mixing phosphoric acid with acetic anhydride (1:9) [6]. The mixture was heated to 65° and stood without heating for 24 hours. Fractionation of the reaction mixture gave methyl 12-acetoxylaurate in quantity of 2 g.

B.p. 168-173° at 3 mm, n_D^{20} 1.4490, e. n. 402.1. $C_{15}H_{28}O_4$. Calculated: e.n. 411.2.

Hydrolysis of this ester gave 12-hydroxylauric acid with m.p. 84-85°. There was no depression of the melting point when this specimen was mixed with the specimen obtained by method a).

Dodecanediol (XI). 35 g of (II) was hydrogenated in presence of 7 g of copper-chromium catalyst at 230-250° and 180 atm with absorption of 10.2 liters of hydrogen (84% of the calculated amount). The catalyst was removed. The neutral portion was separated, and dodecanediol isolated from it in quantity of 6.5 g.

B. p. 175-180° at 3 mm, m. p. 79-81.5° (from benzene). The literature gives m. p. 80-81° [7].
Found %: C 71.39, 71.17; H 12.89, 12.92; OH 16.78. $C_{12}H_{26}O_2$. Calculated %: C 71.23; H 12.95; OH 16.83.

3. Transformations of 3-(ω-carbomethoxyheptyl)-4-hydroxytetrahydropyran

3-(ω-Carbomethoxyheptyl)-4-acetoxytetrahydropyran (XII). 10.5 g of acetyl chloride was added to 20 g of (IV) and 2 g of freshly fused zinc chloride with cooling. At the conclusion of the violent reaction, the mixture was diluted with water and worked up in the usual manner before distillation in vacuo. 8.3 g of (XII) was obtained; yield 35%.

B.p. 190-191° at 3 mm, d_4^{20} 1.0503, n_D^{20} 1.4616, MR_D 78.59; calc. 78.63.
Found %: C 64.19, 63.90; H 9.37, 9.31; e.n. 369.7. $C_{18}H_{32}O_5$. Calculated %: C 63.97; H 9.39; e.n. 372.8.

Methyl 10,12-diacetoxy-9-chloromethyllaurate (XIII). The reaction was performed with twice as much acetyl chloride as in the preceding experiment.* For this purpose, 16 g of acetyl chloride was first added to 31 g of (IV), in analogy with the preceding experiment; then, after completion of the violent reaction (formation of XII), an equal quantity of acetyl chloride (16 g) was added and the mixture heated for an hour at the boil. Fractionation in vacuo gave 13.9 g of (XII) (yield 30.3%) and 7.3 g of (XIII) (yield 20%).

B. p. 205-206° at 3 mm, d_4^{20} 1.100, n_D^{20} 1.4634, MR_D 95.02; calc. 95.19.
Found %: C 57.05, 56.99; H 8.52, 8.30; Cl 9.24; e.n. 588.7. $C_{18}H_{31}O_6Cl$. Calculated %: C 57.09; H 8.25; Cl 9.36; e.n. 591.2.

3-(ω-Carbomethoxyheptyl)-4-benzoxytetrahydropyran (XIV). Reaction of 30 g of (IV) with 16 g of benzoyl chloride in presence of zinc chloride under the same conditions as for preparation of (XII) gave (XIV) in yield of 16 g.

B.p. 218-219° at 6 mm, d_4^{20} 1.0824, n_D^{20} 1.4994, MR_D 98.36; calc. 98.3.
Found %: C 69.82, 69.63; H 8.65, 8.65; e. n. 312.1. $C_{21}H_{30}O_5$. Calculated: C 69.56, H 8.34; e. n. 309.0.

3-(ω-Carbomethoxyheptyl)-4-chlorotetrahydropyran (XV). 36 g of phosphorus pentachloride was added in the course of 20 minutes to 20 g of (IV) in 200 ml of chloroform; the mixture was then heated for 30 minutes on a boiling water bath. The mass was worked up in the usual manner to give 13.6 g of (XV).

B. p. 173-175° at 3 mm, d_4^{20} 1.0682, n_D^{20} 1.4713, MR_D 72.48; calc. 72.81.
Found %: C 60.68, 60.37; H 9.10, 9.85; Cl 13.10; e.n. 212.8. $C_{14}H_{25}O_3Cl$. Calculated %: C 60.70; H 9.10; Cl 12.81; e.n. 404.6.

3-(ω-Carbomethoxyheptyl)-tetrahydro-γ-pyrone (XVI). To a mixture of 23 g of (IV), 25 g of sulfuric acid (d 1.84) and 100 ml of water was added 31 g of sodium dichromate in the course of 45-50 minutes; the mixture was then stirred for 1 hour at 80-85°. Subsequent fractionation of the reaction mixture in vacuo gave 16.5 g of (XVI).

B. p. 175-176° at 3 mm, m. p. 50-51.5°.
Found %: C 65.75, 65.53; H 9.67, 9.72; e. n. 217.9. $C_{14}H_{24}O_4$. Calculated %: C 65.59, H 9.44; e.n. 218.5.

* As in the cleavage of tetrahydropyran described by Synerholm [7].

Semicarbazone with m.p. 132-133° (from alcohol).

Found %: N 13.40, 13.23. $C_{15}H_{27}O_4N_3$. Calculated %: N 13.40.

2,4-Dinitrophenylhydrazone with m.p. 101-102° (from alcohol and then from acetic acid).

Found %: N 12.65, 12.69. $C_{20}H_{28}O_7N_4$. Calculated %: N 12.84.

SUMMARY

1. Condensation of hendecenoic acid with formaldehyde (Prins reaction) is shown to give 4-(ω-carboxyoctyl)-1,3-dioxan (30% of the theoretical), 3-(ω-carboxyheptyl)-4-hydroxytetrahydropyran (16% of the theoretical), and a small quantity of 10-hydroxyhendecanoic acid. It was noted that these compounds are in part present in the reaction mixture in the form of methyl esters.

2. The structures of 4-(ω-carbomethoxyoctyl)-1,3-dioxan and 3-(ω-carbomethoxyheptyl)-4-hydroxytetrahydropyran were confirmed by a series of transformations.

3. It was shown that 4-(ω-carbomethoxyoctyl)-1,3-dioxan can be converted, through a series of steps, into 12-hydroxylauric acid in a yield of about 30%.

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REDUCTION BY FORMIC ACID AND ITS DERIVATIVES

VII. REDUCTION OF COMPOUNDS CONTAINING THE PYRIDINE NUCLEUS

L. G. Yudin, A. N. Kost, Yu. A. Berlin and A. E. Shipov

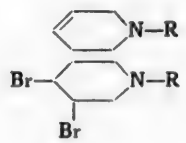
In one of the preceding papers [1] it was shown that the process of reduction of quinolinium salts by formic acid (to 1-alkyl-1,2,3,4-tetrahydroquinolines) is greatly accelerated by addition of triethylamine. In the present work this observation is utilized for reduction of a series of other compounds, containing the pyridine ring.

Reduction of N-alkylpyridinium chlorides or bromides by formic acid in presence of sodium formate [2] leads predominantly to 1-alkylpiperidines, while 1-alkyl-Δ^3-piperideines are only obtained in a yield of 10-15%. On attempting to carry out the reduction of N-ethyl- or N-butylpyridinium iodides by this method, we only obtained unstable iodine-containing bases. But replacement of sodium formate by triethylamine led to equally facile reduction of N-alkylpyridinium chlorides, bromides, iodides and sulfates. The duration of the reaction is shortened from 18-20 to 3-4 hours, and the yields of 1-alkyl-Δ^3-piperideines rises to 25-35%.

Distillation of the mixture of reduced bases in all of the experiments gave a small residue in the flask; this high-boiling fraction evidently consists of products of pairing of pyridine rings. Formation of dipyridyls and of products of their reduction has been noted by many authors who investigated reduction of the pyridine ring [3].

An attempt to reduce pyridine ethobromide with formic acid in presence of pyridine formate (instead of triethylamine formate) by heating for 12 hours was unsuccessful. Many hours' heating of pyridine itself with formic acid and triethylamine or formamide also gave a negative result (the original pyridine was recovered in all cases).

Consequently, N-alkylpyridinium salts are fairly easily reduced with formation of a mixture of 1-alkylpiperidines and 1-alkylpiperideines (I-V). The latter were isolated through the dibromides (VI-X) followed by removal of bromine as described before [2].



R = C_2H_5 (I), n.-C_3H_7 (II), n.-C_4H_9 (III), iso-C_5H_{11} (IV), $C_6H_5CH_2$ (V).

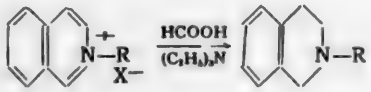
R = C_2H_5 (VI), n.-C_3H_7 (VII), n.-C_4H_9 (VIII), iso-C_5H_{11} (IX), $C_6H_5CH_2$ (X).

Reduction of β-picoline methiodide likewise gave 1,5-dimethyl-Δ^3-piperideine (XI) which was isolated as the dibromide (XII). Some of the prepared compounds were tested for physiological activity. The hydrochloride of (III) was found to be substantially devoid of antibacterial or fungicidal properties.* The hydrochloride of (VI) in 1 : 1000 dilution suppresses the growth of microsporon, achorion and actinomycetes. Hydrochlorides of (IV) and (V) in the same dilution possess tuberculostatic activity. Hydrochlorides of (IX) and (X), also the hydrobromide of (VIII), are somewhat more active; in 1 : 4000 dilution they suppress the growth of cocci,

* Tests were carried out by S. N. Milovanova in the laboratory of Prof. G. N. Pershin (All-Union S. Ordzhonikidze Institute of Pharmaceutical Chemistry).

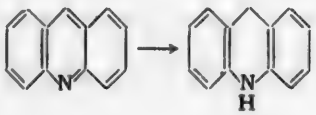
while in 1 : 2000 dilution they inhibit development of acid-resistant bacteria and fungi. According to E. Kh. Zolotarev (Soil Biology Faculty of Moscow University) the hydrochloride of (VI) possesses weak insecticidal activity (in the amount of 1 g/m^2 it kills 50% of the bean aphis and 16% of house flies).

Subsequently we subjected isoquinoline, acridine and their quaternary salts to reduction. Reduction of isoquinoline and its quaternary salts results in hydrogenation of the pyridine ring with formation of 1,2,3,4-tetrahydroisoquinolines. The reaction goes smoothly and without secondary processes; yields reach 80-90%.



It is interesting to note that in contrast to what happens in reduction of quinoline methoiodide [1], when N-methyl-1,2,3,4-tetrahydroquinoline is obtained in 50% yield (due to partial decomposition of the quaternary salt during reaction with formation of N-formyl-1,2,3,4-tetrahydroquinoline), isoquinoline methoiodide gives N-methyl-1,2,3,4-tetrahydroisoquinoline in 86% yield. This is evidently due to the higher basicity of isoquinoline and in turn to the greater stability of its quaternary salts.

In reduction of acridine by formic acid and triethylamine formate, the more labile double bonds of the pyridine ring are attacked, as is usual, and 9,10-dihydroacridine is formed (the formyl derivative of 9,10-dihydroacridine could not be isolated from the reaction mixture).



Acridine methochloride is likewise smoothly converted into N-methyl-9,10-dihydroacridine.

EXPERIMENTAL

Reduction of N-alkylpyridinium salts. 0.25 mole of alkyl halide was added to 0.2 mole of pyridine, and the mixture was refluxed on a water bath until homogeneous. Addition was then made of 46 g (1 mole) of anhydrous formic acid and 40 g (approx. 0.4 mole) of triethylamine, and the mixture boiled for 3-4 hours; after cooling, it was diluted with double the volume of water, and then (with cooling) made strongly alkaline with 40% sodium hydroxide solution. The organic layer was separated and the aqueous layer was extracted 3-4 times with ether. The combined ether extracts and layer of amines was carefully dried with solid caustic alkali and distilled. Ether and triethylamine first came off, followed by a mixture of reduced bases. 2-3 g of high-boiling fraction remained in the flask. Below are given the starting alkyl halides and (in brackets) the percent yields of mixture of bases, calculated on the 1-alkylpyridine: C_2H_5Br (85), C_2H_5I (75.5), $(C_2H_5)_2SO_4$ (69), n-C_3H_7Br (67), n-C_4H_9Br (85), n-C_4H_9I (85.5), iso-$C_5H_{11}Br$ (80), $C_6H_5CH_2Cl$ (67). Yields fell off sharply when the proportion of triethylamine was reduced (to 1 mole amine per mole pyridinium salt). Thus, for example, in the case of ethylpyridinium bromide a mixture of bases in a yield of 16% in all was obtained.

3,4-Dibromo-1-propylpiperidine (VII). Reduction of 0.2 mole of N-propylpyridinium bromide gave 16.7 g of a mixture of reduced bases with b.p. 145-156°. 12.6 g of the hydrochloride of (VII) with m.p. 200.5-201° was obtained by bromination (10 ml of bromine) in 150 ml of concentrated hydrochloric acid followed by evaporation in vacuo and crystallization from anhydrous alcohol [2].

Found %: C 30.01, 30.02; H 4.95, 5.06. $C_8H_{16}NClBr_2$. Calculated %: C 29.88; H 5.01.

The mother liquors were evaporated on a water bath, decomposed with caustic alkali and extracted with ether; the extract was carefully distilled in vacuo on a water bath (receiver cooled with dry ice and acetone) to give 6.5 g (22.5% calculated on the original alkyl halide) of 1-propylpiperidine with b.p. 148-150° (at 753 mm);

picrate with m.p. 121° [4]. Base (VII) remained in the flask. Treatment with hydrochloric acid and recrystallization from anhydrous alcohol yielded the hydrochloride of 3,4-dibromo-1-propylpiperidine (VII) with m.p. 200-200.5°. Total yield 25.6% reckoned on the original pyridine.

From ethyl bromide and pyridine were similarly obtained, after reduction, the hydrochloride of 3,4-dibromo-1-ethylpiperidine (VI) with m.p. 171-172° (yield 30-35%) and 1-ethylpiperidine with b. p. 128-130° (yield 20%). The same dibromide with m.p. 169-170° (yield 30%) was obtained when using diethyl sulfate in place of ethyl bromide. 1-Butylpiperidine with b.p. 168-171° (yield 17.7%) and the hydrochloride of 3,4-dibromo-1-butylpiperidine (VIII) with m.p. 205-206° (yield 36%) were obtained from butyl iodide. Isoamyl bromide gave 1-isoamylpiperidine with b.p. 183-185° (yield 17%) and the hydrochloride of 3,4-dibromo-1-isoamylpiperidine (IX) with m.p. 227° (yield 30-32%). From benzyl chloride and pyridine were similarly obtained 1-benzylpiperidine with b.p. 240-242° (yield 16%) and the hydrochloride of 3,4-dibromo-1-benzylpiperidine (X) with m. p. 190-191° (yield 21%). The constants of the prepared substances agree with those described earlier [2].

Similar reduction of β-picoline in presence of methyl iodide gave N-methyl-β-pipecoline with b. p. 120-123° (at 755 mm) (yield 18%) and the hydrobromide of 3,4-dibromo-1,5-dimethylpiperidine (XII) with m.p. 175° [5] (yield 32.5%).

1-Propyl-Δ^3-piperideine. Prepared by the action of zinc dust on an aqueous solution of the hydrochloride of 3,4-dibromo-1-propylpiperidine (VII), as previously described for other 1-alkyl-Δ^3-piperideines [2]; yield 93-95%.

B. p. 146-148° (at 756 mm), n_D^{20} 1.4605, d_4^{20} 0.8533, MR_D 40.22; calc. 40.51.
Hydrochloride with m.p. 213-214.5° (from anhydrous alcohol).
Found %: N 8.69, 8.88. $C_8H_{16}NCl$. Calculated %: N 8.66.

1,5-Dimethyl-Δ^3-piperideine (XI) was similarly obtained by debromination of the corresponding dibromo compound, b. p. 134-135° (755 mm); picrate with m. p. 107-108° [5].

The preparation of the remaining 1-alkyl-Δ^3-piperideines has already been described [2].

N-Formyl-1,2,3,4-tetrahydroisoquinoline. A mixture of 3.22 g of isoquinoline, 7 ml of triethylamine and 7.6 ml of anhydrous formic acid was refluxed for 7-8 hours; the mass after cooling was made alkaline with concentrated alkali and extracted with ether. The ethereal extract was dried with calcined magnesium sulfate, the ether was distilled off, and the residue distilled in vacuo to give 3.6 g (90%) of N-formyl-1,2,3,4-tetrahydroisoquinoline.

B. p. 150-152° at 6 mm, n_D^{20} 1.5862, d_4^{20} 1.1500, MR_D 47.01, calc. 46.68.

Found %: C 74.33; H 6.91. $C_{10}H_{11}NO$. Calculated %: C 74.50; H 6.87.

Hydrolysis of N-formyl-1,2,3,4-tetrahydroisoquinoline gave 1,2,3,4-tetrahydroisoquinoline in quantitative yield; b. p. 108-109° (at 10 mm); picrate with m.p. 197°; N-phenylisocyanate derivative with m.p. 144-145°; hydrochloride with m.p. 195°. Literature data: b. p. 229-230°; picrate with m.p. 195-196° [6]; hydrochloride with m.p. 197° [7]; N-phenylisocyanate derivative with m.p. 144° [8].

N-Methyl-1,2,3,4-tetrahydroisoquinoline. A mixture of 13.5 g of isoquinoline methoiodide, 14 ml of triethylamine and 15 ml of anhydrous formic acid was refluxed for 10 hours. The mass was then made alkaline with concentrated caustic alkali solution and extracted with ether. The extract was dried with fused caustic alkali, the ether was taken off, and the residue was distilled in vacuo to give 6.3 g (86%) of N-methyl-1,2,3,4-tetrahydroisoquinoline with b.p. 98-100° (at 12 mm). n_D^{20} 1.5406, d_4^{20} 0.9896, MR_D 46.71, calc. 46.79; methoiodide with m.p. 192-194°. Literature data: b.p. 212°; methoiodide with m.p. 189° [9]; ethoiodide with m.p. 132-134° [10].

N-Ethyl-1,2,3,4-tetrahydroisoquinoline. 8-hours' heating of 7.1 g of isoquinoline ethiodide, 7 ml of triethylamine and 10 ml of anhydrous formic acid similarly gave 3.4 g (85%) of N-ethyl-1,2,3,4-tetrahydroisoquinoline with b.p. 96-98° (at 5 mm), n_D^{20} 1.5503, d_4^{20} 0.9919, MR_D 51.77; calc. 51.39; benzyloiodide with m.p. 131-132°; methoiodide with m.p. 139°. A mixed specimen of N-ethyl-1,2,3,4-tetrahydroisoquinoline methoiodide and N-methyl-1,2,3,4-tetrahydroisoquinoline ethoiodide does not show a depression. Literature data: b.p. 225-227° [9]; methoiodide with m.p. 139° [11]; benzyliodide with m.p. 133° [9].

N-Benzyl-1,2,3,4-tetrahydroisoquinoline. Eight hours' boiling of 6.4 g of isoquinoline benzylchloride, 7 ml of triethylamine and 10 ml of anhydrous formic acid gave 3.9 g (70%) of N-benzyl-1,2,3,4-tetrahydroisoquinoline with b.p. 171-173° (at 3 mm); n_D^{20} 1.5991, d_4^{20} 1.0740, MR_D 71.06; calc. 71.12. Methoiodide with m.p. 192-194°. A mixed melting sample of N-methyl-1,2,3,4-tetrahydroisoquinoline benzyliodide and N-benzyl-1,2,3,4-tetrahydroisoquinoline methoiodide does not give a depression. Ethoiodide with m.p. 134°. Literature data: b. p. 194-197° (at 18 mm); ethoiodide with m. p. 133° [9].

Reduction of quinoline methoiodide. Reduction of 13.5 g of quinoline methoiodide with a mixture of formic acid and triethylamine (5-6 hours) gave (after the usual working-up) 3.6 g (50%) of N-methyl-1,2,3,4-tetrahydroquinoline with b.p. 116-120° (at 10 mm); methoiodide with m.p. 174°. In addition 3 g (38%) of N-formyl-1,2,3,4-tetrahydroquinoline was isolated; b.p. 160-165° (at 10 mm) and m.p. 37°. The constants of the prepared compounds agreed with those in the literature [1, 12].

9,10-Dihydroacridine. 2.2 g of acridine, 3.6 ml of triethylamine and 7.6 ml of anhydrous formic acid were refluxed in a flask for 8-9 hours. The mixture was then made strongly alkaline, and the triethylamine was distilled off in vacuo. The precipitate was then collected and recrystallized from aqueous alcohol. Yield 1.7 g (77%) of 9,10-dihydroacridine with m.p. 168°.

Found %: N 7.90, 8.10. $C_{13}H_{11}N$. Calculated %: N 7.72. Literature data: m. p. 170° [13], 168° [14].

9-Methyl-9,10-dihydroacridine. In similar fashion, 1.4 g acridine methochloride, 1.8 ml triethylamine and 7.6 ml of anhydrous formic acid (3-4 hours' heating) gave 1 g (71%) of 9-methyl-9,10-dihydroacridine with m.p. 93-94° (from alcohol). The literature [15] reports m.p. 96°.

Found %: N 7.54, 7.70. $C_{14}H_{13}N$. Calculated %: N 7.17.

SUMMARY

1. Improvements were introduced into the method of preparation of 3,4-dibromo-1-alkylpiperidines and of 1-alkyl-Δ^3-piperideines by reduction of pyridinium salts with formic acid in admixture with triethylamine formate.

2. It was shown that formic acid reduction of isoquinoline and acridine, also of their quaternary salts, leads respectively to 1,2,3,4-tetrahydroisoquinolines and 9,10-dihydroacridines.

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SYNTHESIS OF LEPIDINE BASES FROM ARYLAMINES AND CARBONYL COMPOUNDS

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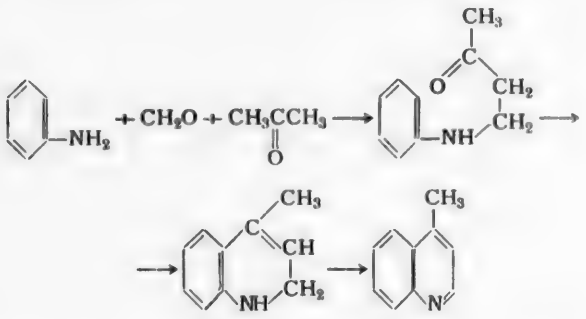
The synthesis of lepidine from aniline, formaldehyde and acetone by the Beyer reaction [1] is an example of an organic reaction that is characterized by many secondary reactions, some of which proceed at high velocity. Pictet and Misner [2] performed the Beyer reaction with various arylamines and were convinced as a result that lepidine and its homologs are formed in yields not exceeding 3-5% of the theoretical. They therefore concluded that the reaction was unsuitable for preparation of γ-derivatives of quinoline. Mikeska [3] slightly modified the Beyer procedure and obtained lepidine in a yield of 4.3%.

After analyzing the main direction of the reaction (formation of butanoneaniline [4]) and a number of secondary directions, we arrived at the conclusion that the Beyer reaction is preferably operated with low concentrations of aromatic amine and formaldehyde in the reaction mixture and in presence of a considerable excess of acetone. We established that lepidine bases are formed in yields of 15-37% from arylamines, formaldehyde and acetone in presence of ferric chloride• and zinc chloride.

The reaction mechanism is the following:



Zinc chloride has no effect on the yield of lepidine bases in synthesis from acetylated amines [5, 6], but in the present case it improves the yield of lepidine and its homologs.

EXPERIMENTAL

Synthesis of lepidine. 60 ml of alcohol, 20 ml of acetone, 50 g of $FeCl_3 \cdot 6H_2O$, 30 ml of concentrated hydrochloric acid, and 5 g of zinc chloride were charged into a round-bottomed flask fitted with reflux condenser and two small burets. In one of the burets were placed 30 ml of aniline, 20 ml of acetone and 10 ml of alcohol; in the other were put a solution of 9.2 g of paraformaldehyde and 60 ml of alcohol.•• The contents of the flask

• An oxidant is not used in the normal Beyer procedure.

•• Paraformaldehyde rapidly dissolves in alcohol on heating in presence of a few drops of hydrochloric acid.

were gently boiled, and every five minutes 2 ml each of the solutions of aniline and paraformaldehyde was run in (alternately from each buret at intervals of 2-5 seconds). After all had been added from the burets, the reaction mixture was boiled for 0.5 hour. The solvent was then distilled off (up to a temperature of 100°), the mixture was made alkaline with 40% sodium hydroxide solution, and the bases were distilled with steam and extracted with benzene. The benzene layer was twice treated in a separating funnel with 50 ml of 10% hydrochloric acid. Lepidine was precipitated from the hydrochloric acid extract with a solution of potassium ferrocyanide [7]. The yellow precipitate was filtered off and decomposed with 5% alkali solution. The resultant oil was extracted with ether, the ether was driven off, and the base distilled at reduced pressure. To the distillate, dissolved in a 5-fold volume of dry ether, was added (stirring) 5 g of pulverized phthalic anhydride in the course of 0.5 hour. After an hour the phthalamic acids were extracted with 10% caustic alkali, and the ether layer was separated and dried with potassium carbonate. Potassium carbonate was then added to the ethereal solution of the base and another 3 g of phthalic anhydride was dissolved in it. After 24 hours, the phthalamic acids were again extracted with caustic alkali. The lepidine was distilled off after the ethereal solution had been dried and the ether driven off. Yield 7 g (15%) of product with b. p. 258-263°, n_D^{20} 1.6182. The picrate of the base melts at 212°. In admixture with an authentic specimen of lepidine picrate the melting point is not depressed.

Found %: N 10.04. $C_{10}H_9N$. Calculated %: N 9.83.

A second experiment was run in the same fashion but in the absence of zinc chloride. 5.4 g (11.7%) of lepidine was obtained.

Synthesis of 6-methyllepidine. From 15 g of p-toluidine and 3.7 g of paraformaldehyde in 30 ml of alcohol was obtained 4.8 g (22%) of 6-methyllepidine with b.p. 267-272°. The picrate of the base melts at 237°, and the melting point of a mixture with an authentic specimen of 6-methyllepidine picrate is not depressed.

Found %: N 9.06. $C_{10}H_{11}N$. Calculated %: N 8.92.

Synthesis of 6,8-dimethyllepidine. The first part of the synthesis was analogous to the preceding syntheses. 15 ml of m-xylidine, 3.8 g of paraformaldehyde and 35 g of $FeCl_3 \cdot 6H_2O$ were brought into reaction. After the flask had been cooled to room temperature, the reaction mixture was diluted with 100 ml of alcohol and made alkaline by stirring with 40% sodium hydroxide (test for alkalinity). The ferrous hydroxide was filtered off, and 25 ml of conc. hydrochloric acid was added to the filtrate. After a few minutes a slurry of crystals of the sparingly soluble hydrochloride of 6,8-dimethyllepidine had formed. The crystals were filtered off and washed with a small quantity of 50% alcohol. From the mother liquor, after evaporation, was isolated an additional small quantity of the hydrochloride of the base.

Decomposition of the salt with 5% sodium hydroxide solution gave 7.8 g (37%) of product with m.p. 56°. After recrystallization from hexane the m. p. rose to 56.5-57°. The picrate of the base melts at 209°.

Found %: N 8.29. $C_{12}H_{13}N$. Calculated %: N 8.20.

SUMMARY

1. Lepidine and its homologs are obtained in yields of 15-37% from arylamines, formaldehyde and acetone in presence of ferric chloride and zinc chloride.

2. The proposed method can be employed for the preparation of considerable quantities of lepidine bases.

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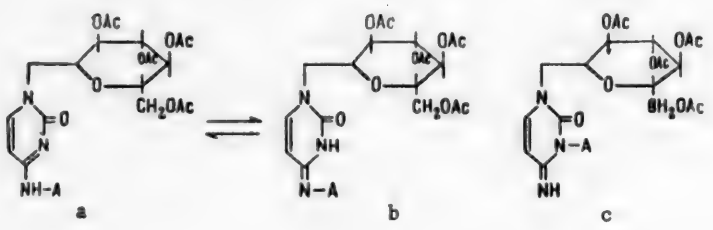
AMINOACYL DERIVATIVES OF NUCLEOSIDES

II. STRUCTURE AND PROPERTIES OF AMINOACYL AND PEPTIDE DERIVATIVES OF 3-β-D-GLUCOPYRANOSYLCYTOSINE

Z. A. Shabarova, N. I. Sokolova and M. A. Prokofyev

The synthesis of aminoacyl and peptide derivatives of 3-β-D-glucopyranosylcytosine was described in the preceding communications [1, 2]. However, the assignment of the structure of N_6-aminoacyl (or peptide) derivatives of 3-β-D-glucopyranosylcytosine (formula a) to the prepared compounds was largely arbitrary. Such a structure does not follow directly from the method of synthesis, and further investigations ere required for establishment of the structure of the compounds. In addition, regarding aminoacyl and peptide derivatives of nucleosides as possible fragments of nucleoproteins, we considered a closer study of the properties of the compounds to be necessary with special reference to the conditions of hydrolysis of the amido bond. The present communication is devoted to these problems.

Taking into consideration the susceptibility of cytosine derivatives to tautomeric transformations, one of the following structures can be assigned to the aminoacyl (or peptide) derivatives of 3-β-D-glucopyranosylcytosine that we synthesized:

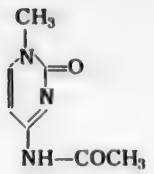


where Ac = CH_3CO

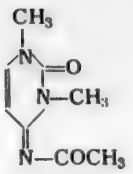
A = acetyl (I)
A = bzr*-glycyl (II)
A = bzr-phenylalanyl (III)
A = bzr-valyl (IV)
A = bzr-valylglycyl (V)
A = bzr-valylphenylalanyl (VI)
A = bzr-valylleucyl (VII)
A = bzr-phenylalanylglycyl-glycyl (VIII)

* bzr = benzene ring.

We attempted to establish the structure of the prepared compounds from analysis of their ultraviolet absorption spectra and by comparing the latter with the absorption spectra of acetyl derivatives of 3-methylcytosine which were studied in detail by Kenner, Reese and Todd [3]. The curves of acetyl (I), aminoacyl and peptide derivatives of 3-β-D-glucopyranosylcytosine (II-VIII) and of acetyl derivatives of 3-methylcytosine (IX and X) are plotted in Figs. 1-3.



(IX)



(X)

Two absorption maxima at λ 250 and 300 mμ are characteristic of all of the derivatives of 3-β-D-glucopyranosylcytosine. The compounds differ only by the intensity of absorption. According to the work of Kenner, Reese and Todd [3], the absorption curve of N_6-acetyl-3-methylcytosine (IX) (Fig. 1) has the same absorption maxima at λ 247 and 300μ, whereas N_6-acetyl-1,3-dimethylcytosine, whose structure corresponds to the tautomeric form b, has an entirely different character of absorption. It follows from comparison of these data that formula a must be assigned to the acetyl, aminoacyl and peptide derivatives that we synthesized.

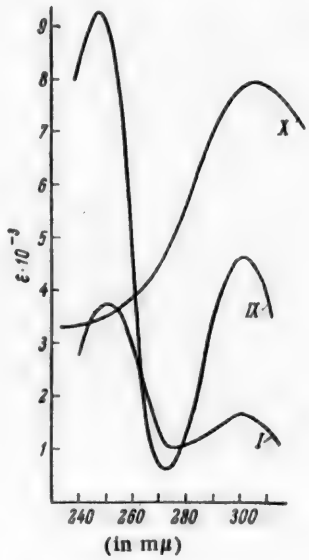


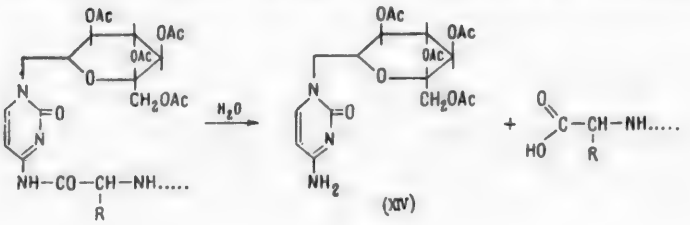
Fig. 1. I) 3-β-D-pentaacetylglucopyranosylcytosine, IX) N_6-acetyl-3-methylcytosine, X) N_6-acetyl-1,3-dimethylcytosine.

Phthalyl-substituted N_6-aminoacyl derivatives of cytosine nucleoside [2], as evident from the curves in Fig. 4, have a slightly different absorption. The absorption maximum at λ 300μ remains the same, but the first maximum is shifted farther toward the short-wave region. A large number of phthalyl groups causes a larger shift of the first maximum into the short-wave region.

Derivatives of 3-β-D-glucopyranosylcytosine with an unsubstituted amino group have a characteristic absorption curve (Fig. 5). They have one maximum at λ 275 mμ. Comparison of the absorption curves of N_6-acyl derivatives of 3-β-D-glucopyranosylcytosine (compounds (I-VIII) with the curves of 3-β-D-glucopyranosylcytosine (XIII) and 3-β-D-tetraacetylglucopyranosylcytosine (XIV) indicate that passage of the amino group in a cytosine nucleoside from the free state to a blocked acyl group, and conversely, each time involves a change in the character of the ultraviolet absorption. The presence of acetyl groups in a sugar ring (Fig. 5) does not influence the character of the absorption of nucleosides.

We made use of the fact that a cytosine nucleoside with a free amino group (Fig. 5) has an absorption curve in the ultraviolet sharply differing from the absorption curves of its N_6-aminoacyl derivatives (Figs. 2 and 3) for study of the course of hydrolysis of the amido bond in the latter.

Assuming that hydrolysis results only in rupture of the amido bond and with formation of 3-β-D-tetraacetylglucopyranosylcytosine (XIV) and of bzr-aminoacid or bzr-peptide, we investigated the absorption in the ultraviolet of an equimolar mixture of 3-β-D-tetraacetylglucopyranoylcytosine and bzr-valylphenylalanine. This curve should correspond to the absorption curve of the



hydrolyzate of N_ε-bzr-valylphenylalanyl-3-β-D-tetraacetylglycopyranosylcytosine (VI) if its hydrolysis proceeded to the extent of 100%. It was found that the absorption maximum of this mixture is in the 275 mμ region, just like that of the original nucleoside with a free amino group (Fig. 5). Consequently, the presence of bzr-peptide does not influence the character of the absorption of a cytosine nucleoside.

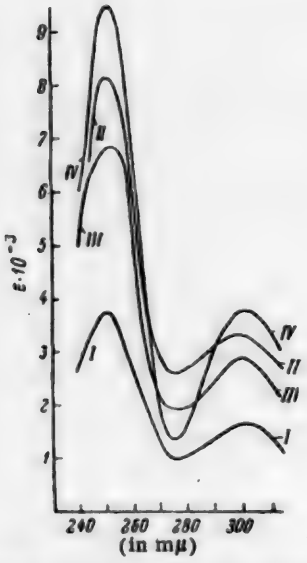


Fig. 2. I) 3-β-D-pentaacetylglucopyranosylcytosine, II) bzr-glycyl-3-β-D-tetraacetylglucopyranosylcytosine, III) bzr-phenylalanyl-3-β-D-tetraacetylglucopyranosylcytosine, IV) bzr-valyl-3-β-D-tetraacetylglucopyranosylcytosine.

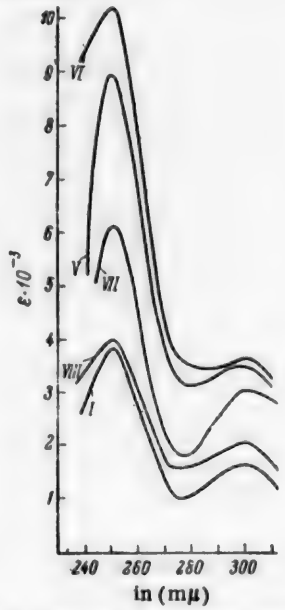


Fig. 3. I) 3-β-D-pentaacetylglucopyranosylcytosine, V) bzr-valylglycyl-3-β-D-tetraacetylglucopyranosylcytosine, VI) bzr-valylphenylalanyl-3-β-D-tetraacetylglucopyranosylcytosine, VII) bzr-valylleucyl-3-β-D-tetraacetylglucopyranosylcytosine, VIII) bzr-phenylalanylglycylglycyl-3-β-D-tetraacetylglucopyranosylcytosine.

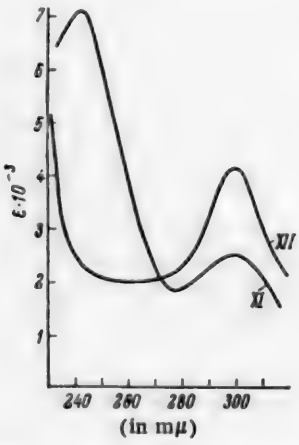


Fig. 4. XI) phthalylglycyl-3-β-D-tetraacetylglucopyranosylcytosine, XII) pentaphthalylglycyl-3-β-D-glucopyranosylcytosine.

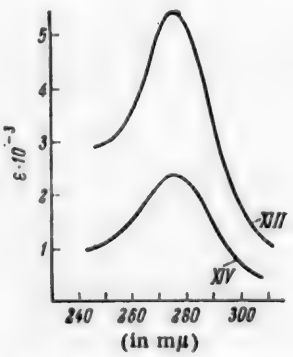


Fig. 5. XIII) 3-β-D-glucopyranosocytosine XIV) 3-β-D-tetraacetylglucopyranosylcytosine.

We also plotted the ultraviolet absorption spectra of mixtures of N_6-acylated nucleoside and of the products of its hydrolysis (an equimolar mixture of 3-β-D-tetraacetylglucopyranosylcytosine and the corresponding bzr-aminoacid or peptide). The absorption maxima of such mixtures were in the 250-275 mμ region. The presence of even an insignificant quantity of unreacted N_6-aminoacylnucleoside was always accompanied by shift of the absorption maximum from 275 mμ toward shorter wavelengths with formation of a new maximum in the 300 mμ region.

Aqueous, acid and alkaline hydrolysis of all of the synthesized compounds was undertaken [1, 2]. N_6-bzr-Aminoacyl (and peptide) derivatives of the cytosine nucleoside were found to be fairly resistant to the hydrolytic action of water. Thus, boiling of N_6-bzr-phenylalanyl-3-β-D-tetraacetylglucopyranosylcytosine (III) with water for 50 hours did not lead to breakdown of this compound.

Alkaline hydrolysis was effected by boiling N_6-aminoacyl and N_6-peptide derivatives of the cytosine nucleoside with 0.1 N NaOH. Table 1 gives the absorption maxima in the UV of the hydrolyzates in dependence on the duration of hydrolysis.

TABLE 1

Absorption Maxima (in mμ) of Hydrolyzates in Dependence on Duration of Alkaline Hydrolysis

Name of compound	Duration of hydrolysis (in minutes)				
	15	30	50	60	80
N_6-bzr-Glycyl-3-β-D-tetraacetylglucopyranosylcytosine (II)	255	260	265	275	—
N_6-bzr-Phenylalanyl-3-β-D-tetraacetylglucopyranosylcytosine (III)	260	260	260	—	275
N_6-bzr-Valyl-3-β-D-tetraacetylglucopyranosylcytosine (IV)	260	260	275	—	—
N_6-bzr-Valylglycyl-3-β-D-tetraacetylglucopyranosylcytosine (V)	265	275	—	—	—
N_6-Valylphenylalanyl-3-β-D-tetraacetylglucopyranosylcytosine (VI)	260	265	275	—	—
N_6-bzr-Valylleucyl-3-β-D-tetraacetylglucopyranosylcytosine (VII)	265	265	—	275	—

It follows from the data of this table that the nature of the aminoacyl residue affects the resistance of the amino bond. Thus, phenylalanyl derivatives are hydrolyzed with great facility; on the other hand, valylglycyl derivatives are hydrolyzed with comparative difficulty.

Formation of free bzr-aminoacid or bzr-peptide during hydrolysis was demonstrated by chromatographic examination of the hydrolyzates in a butanolammonia medium. The chromatograms were developed by wetting with starch-KI-KIO_3 mixture [4]. Lilac spots appeared at the zones of location of the bzr-aminoacids or bzr-peptides. This technique was applied to the detection of bzr-phenylalanine and bzr-valylleucine in the hydrolyzates of the appropriate N_6-derivatives of cytosine nucleosides.

EXPERIMENTAL

1. Plotting of Absorption Spectra of 3-β-D-Glucopyranosylcytosine and Its Derivatives in the Ultraviolet

Absorption curves in the 230-320 mμ region were plotted with the SF-4 spectrophotometer. Optical densities were measured at intervals of 3 mμ, and in the region of the maximum and minimum at intervals of 1 mμ. The graphs shown in Figs. 1-5 were plotted on the basis of the data obtained. Solutions of the compounds in 96% alcohol were used in making observations. When a compound was isolated as the hydrochloride and it was necessary to plot the absorption curve of the base, the hydrochloride was dissolved in the minimum amount of

water, and the solution was neutralized (neutral reaction using a universal indicator) and diluted with anhydrous alcohol.

TABLE 2

Absorption Maxima (in mμ) of Hydrolyzates in Dependence on Duration of Acidic Hydrolysis

Name of compound	Concentration of hydrochloric acid (normality)	Duration of hydrolysis (in minutes)	Absorption maximum of hydrolyzate (in mμ)
N_6-bzr-Glycyl-3-β-D-tetraacetylglucopyranosylcytosine (II)	0.1	120	260
	1	120	255—260
	2	20	275
N_6-bzr-Phenylalanyl-3-β-D-tetraacetylglucopyranosylcytosine (III)	0.1	15	275
N_6-bzr-Valyl-3-β-D-tetraacetylglucopyranosylcytosine (IV)	0.1	120	250—255
	1	60	260—265
	2	20	275
N_6-bzr-Valylglycyl-3-β-D-tetraacetylglucopyranosylcytosine (V)	2	60	275
N_6-bzr-Valylphenylalanyl-3-β-D-tetraacetylglucopyranosylcytosine (VI)	0.1	60	255—260
	1	60	275
N_6-bzr-Valylleucyl-3-β-D-tetraacetylglucopyranosylcytosine (VII)	2	20	275

2. Hydrolysis of N_6-Aminoacyl and Peptide Derivatives of 3-β-D-tetraacetylglucopyranosylcytosine

Aqueous, acidic and alkaline hydrolysis of compounds (II) to (VII) was effected by dissolving 15-20 mg of compound in 2.5 ml of water, alkali solution or acid in a 5 ml graduated test tube to which a reflux condenser was attached through a ground-glass connection. The solution was heated to the boil over a bare flame. After definite intervals of time 0.2 ml samples were withdrawn (using a micropipet) and diluted to 5 ml with anhydrous alcohol in a small measuring flask. The solution was then examined for its UV absorption. For the purpose of hydrolysis with acid or alkali, the compound was first neutralized (using a universal indicator) and then diluted with anhydrous alcohol to such a volume that a solution of the compound in 96% alcohol was obtained. Data for acidic and alkaline hydrolysis of derivatives of cytosine nucleoside are presented in Tables 1 and 2. The absorption maxima of aqueous hydrolyzates of the compounds listed above were located in the 255-260 and 300 mμ regions and did not change with duration of heating (up to 50 hours); this demonstrated that the amido bond was not cleaved under these conditions.

Formation of a bzr-amino acid or bzr-peptide of the cytosine nucleoside during acidic or alkaline hydrolysis of N_6-bzr-aminoacyl and bzr-peptide derivatives was demonstrated by paper chromatography. For this purpose, the hydrolyzate (pH 5-6) was chromatogrammed in a butanol-ammonia medium [4]. The chromatogram was dried for 30 minutes at 140° and wetted with a mixture comprising starch, 1 N KI and 1 N KIO_3 (1:1:1). Lilac stains were developed at the positions occupied by the bzr-amino acids and bzr-peptides. bzr-Phenylalanine (R_f 0.73) and bzr-valylleucine (R_f 0.58) were detected in the acidic and alkaline hydrolyzates of the corresponding N_6 derivatives of the cytosine nucleoside.

SUMMARY

1. It was shown that reaction of aminoacylated cytosine nucleoside with mixed anhydrides of bzr-amino acids and bzr-peptides gives N_6-aminoacyl and N_6-peptide derivatives of the nucleoside (its amino group is acylated).

2. It was established that the amido bond in N_6-bzr-aminoacyl and N_6-bzr-peptide derivatives of the cytosine nucleoside is resistant toward the hydrolytic action of water, is hydrolyzed with difficulty by acid,

and hydrolyzed with relative facility by caustic alkali. A relation between the rate of hydrolysis and the nature of the aminoacyl residue forming the amido bond was established.

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THE THERMAL ISOMERIZATION OF ALLYLARYL SULFIDES

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A characteristic property of allylaryl ethers is the Claisen rearrangement – the ability of these ethers to isomerize on heating to form o-allylphenols [1]. The objective of the present work was a study of the thermal isomerization of sulfur analogs of allyl ethers – allylphenyl sulfide and o- and p-allyltolyl sulfides.

Hurd and Greengurd [2] carried out the pyrolysis of allylphenyl and allyl-p-tolyl sulfides. They assumed that both of the sulfides undergo the Claisen rearrangement with formation of about 25% of o-allylthiophenol and 2-allyl-4-methylthiophenol respectively. Without refuting these results, Tarbell and McCall [3] point out that allylphenyl sulfide does not alter when boiled with tributylamine (i.e. at 216°). Petropoulos [4] later showed in collaboration with the preceding authors that the Claisen rearrangement is markedly inhibited in the case of derivatives of allylphenyl sulfide whose oxygenated analogs isomerize under mild conditions; in no case did these authors observe the formation of the corresponding allylthiophenols.

Unlike Hurd and Greengurd, we established that allylthiophenol is substantially not formed when allylphenyl sulfide is boiled without a solvent, but propenylphenyl sulfide is formed; the latter is identical with the product isolated by Tarbell and McCall [3] by the action of an alcoholic solution of sodium alkoxide on allylphenyl sulfide.

$$C_6H_5—S—CH_2—CH=CH_2 \xrightarrow{t^\circ} C_6H_5—S—CH=CH—CH_3$$

Propenylphenyl sulfide forms products of condensation on standing or on heating. The product assumed [2] to be o-allylthiophenol was presumably a mixture of products of condensation of propenylphenyl sulfide containing a certain amount of monomer and only traces of allylthiophenol, which had never hitherto been obtained. The structure of the product of thermal isomerization of allylphenyl sulfide was established by hydrogenation over Raney Ni, which proceeds according to the equation:

$$C_6H_5—S—CH=CH—CH_3 \xrightarrow{H_2(Ni)} \text{C}_6\text{H}_{11}\text{SH} + CH_3CH_2CH_3 + H_2S$$

Oxidation of propenylphenyl sulfides gives two sulfones which are probably cis-trans-isomers.

Infrared absorption spectra of allylphenyl sulfide and of the product of its thermal isomerization were plotted.•

The spectrum of allylphenyl sulfide is in satisfactory agreement with the spectrum obtained in a narrower region (1000-15000 cm^{-1}) by Schreiber [5]. As had been expected, the spectrum that we obtained for propenylphenyl sulfide did not contain the absorption band characteristic of the SH-group, thus demonstrating the absence of even traces of allylthiophenol. The absorption spectrum of propenylphenyl sulfide described by Tarbell and McCall [3] for the 650-1600 cm^{-1} region is substantially identical with the spectrum of our isomerization product.

• The spectra were obtained by Yu. N. Sheinker in the optical laboratory of the S. Ordzhonikidze Institute of Pharmaceutical Research.

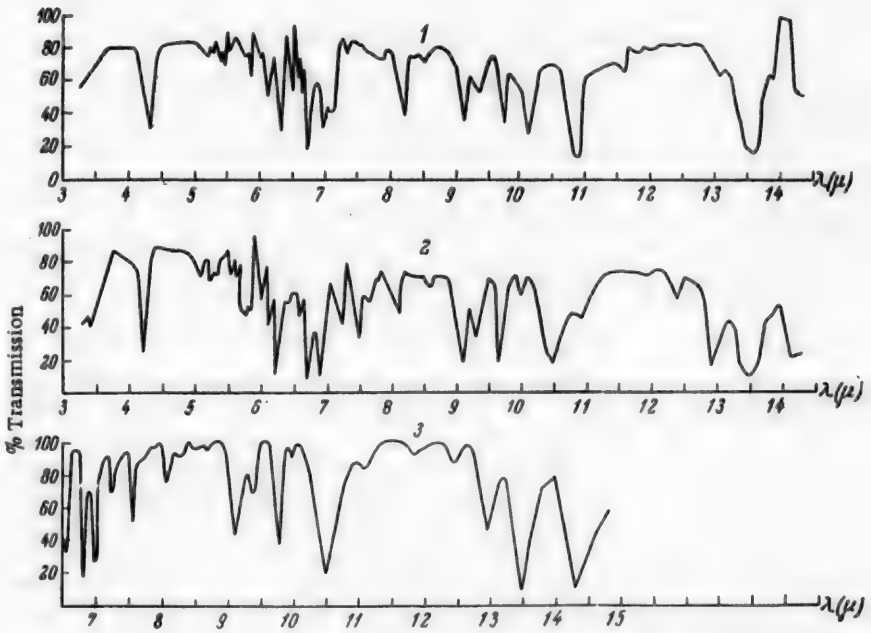
Thermal isomerization of allyl-o- and -p-tolyl sulfides takes a course similar to that of allylphenyl sulfide, with formation respectively of propenyl-o- and -p-tolyl sulfide; neither allyl-p-thiocresol (contrary to the claim in [2]) nor allyl-o-thiocresol are formed. We also obtained propenyltolyl sulfides by heating the corresponding allyltolyl sulfides with an alcoholic solution of sodium ethoxide. The structure of the products of isomerization was established on the basis of hydrogenolysis over Raney Ni: in all cases toluene and propane were isolated.

The data that we obtained enabled us to conclude that allylaryl thioethers differ from the corresponding oxygen-containing compounds in not undergoing the Claisen rearrangement; this is evidently associated with the deactivating influence of sulfur on the process of electrophilic substitution of the aromatic ring.

Both allylphenyl sulfide and propenylphenyl sulfide are decomposed under the action of an alcoholic solution of $HgCl_2$ with formation of thiophenol mercurichloride; the reaction is analogous with the cleavage of arylthiovinyl ethers [6]:

$$C_6H_5S{-}CH_2CH{=}CH_2 + HgCl_2 + 2C_2H_5OH \rightarrow C_6H_5SHgCl + HCl + C_7H_{16}O_2$$
$$C_6H_5SCH{=}CHCH_3 + HgCl_2 + 2C_2H_5OH \rightarrow C_6H_5SHgCl + HCl + C_7H_{16}O_2$$

Determination of the quantity of HCl released showed that this reaction differs from that the thiovinyl ethers in not proceeding to completion.



Infrared absorption spectra of allylphenyl sulfide and propenylphenyl sulfide.
1) Allylphenyl sulfide; 2) product of thermal isomerization of allylphenyl sulfide; 3) propenylphenyl sulfide – data of Tarbell and McCall [3].

EXPERIMENTAL

(with participation of L. D. Aristova)

Synthesis of the Starting Sulfides

Allylphenyl sulfide was obtained, as described in [2], from sodium thiophenate and allyl bromide in alcohol.

After distillation in a 25-plate column with Fenske glass packing, the product had the following characteristics:

B.p. 47.3-47.9° (0.2 mm), 75.3° (3 mm), 114° (25 mm), 220.5-221° (742 mm); m.p. −48-46.5°, • n_D^{20} 1.5755, d_4^{20} 1.0257, MR_D 48.44; calc.•• 47.59. EMR_D 0.85.
Found %: C 72.05; H 6.77; S 21.26. M••• 147.3. $C_9H_{10}S$. Calculated %: C 72.00; H 6.67; S 21.34. M 150.

The paper of Hurd and Greengurd [2] erroneously gives b.p. 104-106° (25 mm), 215-218° (750 mm), $n_D^{20.6}$ 1.4772. Constants of allylphenyl sulfide [8]: b. p. 48-49° (0.43 mm), n_D^{25} 1.5732, d_4^{25} 1.0220, MR_D 48.46, EMR_D 0.97.

Allylphenyl sulfide slowly forms a complex with a 5-fold excess of $HgCl_2$ in alcohol; decomp. p. 191-192° (from alcohol); a mixture with thiophenol mercurichloride [9] melts at 191-192°. Decomposition of this complex with 15% HCl and steam gave thiophenol (b.p. 166.5-167.5°, n_D^{20} 1.5905).

Allyl-o-tolyl sulfide was similarly obtained, starting from o-thiocresol [b.p. 102.5-103° (45.5 mm), n_D^{20} 1.5650, d_4^{20} 1.0512]. Yield of allyl-o-tolyl sulfone 90%.

B.p. after redistillation from a Claisen flask) 96-97° (5 mm), n_D^{20} 1.5707, d_4^{20} 1.0125, MR_D 53.19; calc. 52.23. EMR_D 0.96.
Found %: C 73.17; H 7.42; S 19.04. M 163.5. $C_{10}H_{12}S$. Calculated %: C 73.17; H 7.32; S 19.51. M 164.

6 g of allyl-o-tolyl sulfide was dissolved in 75 ml of acetic acid and oxidized with 18 ml of 27% H_2O_2; the reaction mixture was heated for 1 hour at 100°, the solvent was driven off at the same temperature in vacuo. The residue was diluted with water and extracted with benzene, and the combined extracts were dried and distilled in vacuo. Allyl-o-tolyl sulfone was isolated; yield 61%, b.p. 168-170° (8 mm), n_D^{20} 1.5492, d_4^{20} 1.1673.

Found %: C 61.42; H 6.17; S 16.17. $C_{10}H_{12}O_2S$. Calculated %: C 61.22; H 6.12; S 16.32.

Allyl-p-tolyl sulfide. Prepared in similar fashion to the preceding compound from p-thiocresol and allyl bromide; yield 86%.

After redistillation from a Claisen flask it had b.p. 127-128° (25 mm), n_D^{20} 1.5665, d_4^{20} 1.0042, MR_D 58.31; calc. 52.23. EMR_D 1.08.
Found %: C 73.01; H 7.30; S 19.05. M 161.7. $C_{10}H_{12}S$. Calculated %: C 73.17; H 7.32; S 19.51. M 164.

Allyl-p-tolylsulfone was prepared, m.p. 50.5-51°. Constants of allyl-p-tolylsulfide [2]: b.p. 123-127° (25 mm), n_D^{21} 1.5711; melting point of allyl-p-tolylsulfone 52-53° [10].

Thermal Isomerization of Allylaryl Sulfides

Allylphenyl sulfide. 150 g of allylphenyl sulfide was refluxed in a nitrogen stream for 9 hours. After this period the boiling point of the mixture had risen to 234° and the n_D^{19} to 1.5910. The small quantity of mercaptans formed at the same time was removed by treating the mixture many times with 20% NaOH solution; this treatment removed the unpleasant smell from the organic layer. The aqueous-alkaline layer was collected, acidified with HCl and extracted with ether. After removal of the ether, the residue was treated with an alcoholic solution of $Pb(CH_3COO)_2$ until precipitation was complete. 0.19 g of lead mercaptide was isolated. The organic layer, separated from the aqueous-alkaline layer, was diluted with ligroine, washed free of alkali, and dried with calcined $MgSO_4$. The residue, after removal of solvent, was distilled in the column used for isolation of allylphenyl sulfide to give 40 g of unreacted allylphenyl sulfide and 39.7 g of propenylphenyl sulfide (yield 36%, reckoned on the reacted allylphenyl sulfide).

B. p. 79-80° (3 mm), 225-226° (740 mm), n_D^{20} 1.5850, d_4^{20} 1.0328, MR_D 48.75; calc. 47.59. EMR_D 1.16.
Found %: C 72.04; H 6.68; S 21.32. $C_9H_{10}S$. Calculated %: C 72.00; H 6.67; S 21.34.

• The melting point of allylphenyl sulfide was determined thermographically by N. A. Nechitailo.
•• Molecular refractions were calculated from bond refractions [7].
••• Molecular weights were determined by the cryoscopic method in benzene.

Constants of propenylphenyl sulfide [3]: b.p. 61-69° (1.3 mm), n_D^{20} 1.5850.

Freshly distilled propenylphenyl sulfide was found to have M 145 (calc. 150); after a week the molecular weight had risen to 183. The residue after distillation of the monomer from the product (a yellowish oil) boils over a wide range and at the end with decomposition; its sulfur content is the same as that of the monomer (21.31%) but the $n_D^{20.5}$ is 1.6023 and the M is 244; consequently the dimer content of the residue is approx. 63%. The residue, like propenylphenyl sulfide itself, does not give a precipitate with $Pb(CH_3COO)_2$. After prolonged standing the polymerized residue becomes more viscous and gradually decomposes with liberation of diphenyl sulfide; m.p. 59.5-60.5° (from alcohol; no depression in admixture with an authentic specimen). Treatment of propenylphenyl sulfide with a 5-fold excess of an alcoholic solution of $HgCl_2$ causes rapid precipitation of the mercurichloride with decomp. p. 191-192° (from alcohol). The mercurichloride does not give a depression of melting point in admixture with the mercurichloride prepared from allylphenyl sulfide or with thiophenol mercurichloride.

Found %: C 20.96; H 1.56. C_6H_5SHgCl. Calculated %: C 20.86; H 1.45.

1 g of propenylphenyl sulfide in 15 ml of glacial acetic acid was oxidized with a 200% excess of 28% H_2O_2 for 1 hour at 100°. The reaction mixture was diluted with water to about 200 ml and evaporated to about 50 ml, again diluted and evaporated (5 times in all), after which it was cooled with a mixture of ice and salt. Propenylphenyl sulfone was isolated; weight (unpurified) 0.3 g, m. p. 68-69° (from 4:1 alcohol-water mixture).

Found %: C 59.36; H 5.46; S 17.70. $C_9H_{10}O_2S$. Calculated %: C 59.34; H 5.49; S 17.58.

Hydrogenolysis.• 20 g of propenylphenyl sulfide in 112 ml alcohol was stirred at the boil for 8 hours with Raney Ni prepared as described in [11] from 70 g of Raney alloy. The evolved gases were collected in a Mariotte bottle and analyzed. 278 ml (96%) of propane was obtained. The reaction mixture was diluted with 50 ml of water and distilled off from the Ni and NiS. The distillate was distilled in a column 38 cm high containing Levin fine metal packing.

The fractions, containing an azeotropic mixture with b.p. 64.5-77°, were diluted with water; 0.5 ml (42%) of benzene was isolated; it was identified by the ultraviolet absorption spectrum.••

Allyl-o-tolyl sulfide. 12 g of allyl-o-tolyl sulfide was refluxed for 3 hours; after this period the boiling point of the mixture had risen from 242 to 251.5°. The reaction mixture was treated in the same manner as in the case of allylphenyl sulfide. Redistillation from a Claisen flask gave 6.15 g (51.2%) of propenyl-o-tolyl sulfide.

B. p. 129-133° (25 mm), n_D^{20} 1.5762, d_4^{20} 1.0175, MR_D 53.35; calc. 52.23. EMR_D 1.12.
Found %: C 73.32; H 7.29; S 19.91. $C_{10}H_{12}S$. Calculated %: C 73.17; H 7.32; S 19.51.
The product did not give a precipitate with $Pb(CH_3COO)_2$.

3 g of propenyl-o-tolyl sulfide in 45 ml of acetic acid was oxidized with 9 g of 27% H_2O_2 for 1 hour at 100°. The reaction mixture was worked up in the same manner as in the oxidation of allyl-o-tolyl sulfide. Propenyl-o-tolyl-sulfone was obtained; yield 2.5 g.

B. p. 173-175° (7 mm), n_D^{20} 1.5551, d_4^{20} 1.1741.
Found %: C 61.24; H 6.15; S 16.43. $C_{10}H_{12}O_2S$. Calculated %: C 61.22; H 6.12; S 16.32.

Reduction of 5 g of propenyl-o-tolyl sulfide with Raney Ni (from 140 g of Raney alloy) in 280 ml of alcohol gave 1.9 g (78%) of toluene, b. p. 107-109°, n_D^{21} 1.4910.

Allyl-p-tolyl sulfide. 7.20 g of allyl-p-tolyl sulfide was refluxed for 3 hours, the boiling point of the reaction mixture rising from 240 to 255°; $n_D^{19.5}$ at the end of the reaction was 1.5858. Partial decomposition was observed, and approx. 0.33 g of propylene was isolated. The reaction mixture was worked up as described above. Redistillation from a Claisen flask gave propenyl-p-tolyl sulfide; yield 36.8%.

B. p. 131-136° (25 mm), n_D^{20} 1.5746, d_4^{20} 1.0119, MR_D 53.52; calc. 52.23. EMR_D 1.29.

• The procedure described below was employed for dehydrogenation of all of the products of isomerization.
•• Measured by M. V. Shishkina and M. B. Serebrennikova in the laboratory of petroleum physics and physical chemistry of our institute.

The product does not give a precipitate with $Pb(CH_3COO)_2$; after the distillation the high-boiling fractions in the residue contained only traces of compounds with the SH group.

1 g of propenyl-p-tolyl sulfide in 15 ml of acetic acid was oxidized with 3 g of 27% H_2O_2 as described above. To the reaction mixture was added 200 ml of water; after about 12 hours the sulfone came down, weight 0.67 g; a further 0.15 g was isolated from the mother liquor. The melting point of propenyl-p-tolyl sulfone was 97.5-98.5° after numerous recrystallizations from a mixture of alcohol and benzene.

Found %: C 61.26; H 6.06; S 16.51. $C_{10}H_{12}O_2S$. Calculated %: C 61.22; H 6.12; S 16.32.
According to [12] the melting point of propenyl-p-tolylsulfone is 99-100°.

6 g of propenyl-p-tolyl sulfide was reduced with Raney Ni (from 160 g of Raney alloy) in 300 ml of alcohol, 654 ml (81%) of propane and 1.4 g (44%) of toluene were isolated; b.p. of the latter 105-109°, $n_D^{22.5}$ 1.4779.

Isomerization of Allylaryl Sulfides Under the Action of Sodium Ethoxide

Allylphenyl sulfide. 8 g of allylphenyl sulfide was heated with an alcoholic solution of sodium ethoxide as described in [3]. Propenylphenyl sulfide was obtained; yield 87.7%; b.p. (after redistillation from a Claisen flask) 101-102° (13-13.5 mm), 113-114° (24 mm), $n_D^{20.5}$ 1.5832. 5 g of propenylphenyl sulfide was oxidized with H_2O_2 as described above to give propenylphenyl sulfone, m.p. 68.5-69° (from alcohol); yield 34.1%. A mixture with the sulfone obtained by oxidation of the product of thermal isomerization of allylphenyl sulfide did not give a depression of melting point. The mother liquors after separation of the solid propenylphenyl sulfone probably the trans-isomer were combined and extracted with benzene; the benzene extract was washed with water, dried and distilled in vacuo. A liquid propenylphenyl sulfone (probably the cis-isomer) was isolated; yield 1.22 g (17.0%).

B. p. 176-180° at 3.5 mm (bath temperature), $n_D^{21.5}$ 1.5536.
Found %: C 59.31; H 5.55; S 17.54. $C_9H_{10}O_2S$. Calculated %: C 59.34; H 5.38; S 17.58.

Allyl-o-tolyl sulfide. 16 g of allyl-o-tolyl sulfide and 200 ml of alcohol containing 7 g of sodium in solution were refluxed in a nitrogen atmosphere for 12 hours. The reaction mixture was poured into 1000 ml of cooled water and extracted with ether. The ethereal extracts were combined, washed with water, dried with $MgSO_4$, and distilled to give propenyl-o-tolyl sulfide; yield 83.7%.

B.p. (after redistillation from a Claisen flask) 129.5-134° (25 mm), n_D^{20} 1.5782, d_4^{20} 1.0184, MR_D 53.46; calc. 52.23. EMR_D 1.23.
Found %: C 73.25; H 7.35; S 19.50. M 164.1. $C_{10}H_{12}S$. Calculated %: C 73.17; H 7.32, S 19.51. M 164.

The sulfone obtained by oxidation of this product had b.p. 175-176° (8 mm), n_D^{20} 1.5562, d_4^{20} 1.1750.

Found %: C 61.30; H 6.16; S 16.35. $C_{10}H_{12}O_2S$. Calculated %: C 61.22; H 6.12; S 16.32.

6 g of the product of isomerization in 300 ml of alcohol was boiled for 12 hours with Raney Ni (from 160 g of alloy). 2.15 g (80%) of toluene was isolated; b.p. 108-109°, $n_D^{19.5}$ 1.4905.

Allyl-p-tolyl sulfide. From 8 g of allyl-p-tolyl sulfide, using the above procedure, was obtained propenyl-p-tolyl sulfide; yield 85%.

B. p. 131-135° (25 mm), n_D^{20} 1.5746, d_4^{20} 1.0129, MR_D 53.47; calc. 52.23. EMR_D 1.24.
Found %: C 73.24; H 7.32; S 19.43. M (for freshly distilled sulfide) 163.5. $C_{10}H_{12}S$. Calculated %: C 73.17; H 7.32; S 19.51. M 164. (After 6 months the molecular weight had risen to 172.)

Propenyl-p-tolyl sulfone: m.p. 97.5-98°; a mixture with the corresponding product of thermal isomerization did not give a depression of melting point.

3 g of propenyl-p-tolyl sulfide was reduced over Raney Ni as described above and gave 0.8 g of toluene.

The color reaction with sulfuric acid is characteristic of all of the propenylaryl sulfides that we studied. To a drop of propenylaryl sulfide was added 2 drops of conc. H_2SO_4; a red color appeared which quickly changed to brown. Allylphenyl and allyltolyl sulfides only give a faint yellow color when conc. H_2SO_4 is added.

SUMMARY

1. In the allylaryl thioether series thermal isomerization with formation of allylthiophenols (Claisen rearrangement) substantially does not take place. This is in contrast to the behavior of the corresponding oxygen-containing compounds.

2. Heating of allylaryl sulfides results in isomerization to the corresponding propenylaryl sulfides.

3. The following were prepared for the first time: allyl-o-tolyl sulfide, allyl-o-tolylsulfone, propenyl-o- and -p-tolyl sulfides, propenyl-o-tolyl sulfone, cis- and trans-propenylphenyl sulfones.

4. Allylphenyl sulfide and propenylphenyl sulfide are cleaved by an alcoholic solution of $HgCl_2$ with formation of thiophenol mercurichloride.

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HALOARYLATION OF UNSATURATED COMPOUNDS WITH AROMATIC DIAZO COMPOUNDS

VI. THE ABSORPTION SPECTRA IN THE ULTRAVIOLET AND VISIBLE REGIONS OF ARYLBUTENES, ARYLBUTADIENES AND ARYLBUTENYNES

N. B. Kupletskaya, A. V. Dombrovsky and A. P. Terentyev

The method of chloroarylation developed for butadiene-1,3, its homologs and analogs makes it possible to prepare chloroarylbutenes simply and in 50-70 % yields [1]. These compounds are synthesized by reacting appropriate dienes and diazotized aromatic amines in an aqueous acetone solution in the presence of a catalyst (cupric chloride). Of the many reactions that chloroarylbutenes may undergo, the elimination of hydrogen chloride to form the corresponding α-arylbutadienes was found to be the most interesting. A method was developed for the elimination of hydrogen chloride using powdered potassium hydroxide, in dioxan [2]. Analogously, the reaction products of diazotized aromatic amines and vinylacetylene gave arylbutenynes of the type $XC_6H_4CH=CH-C\equiv CH$.

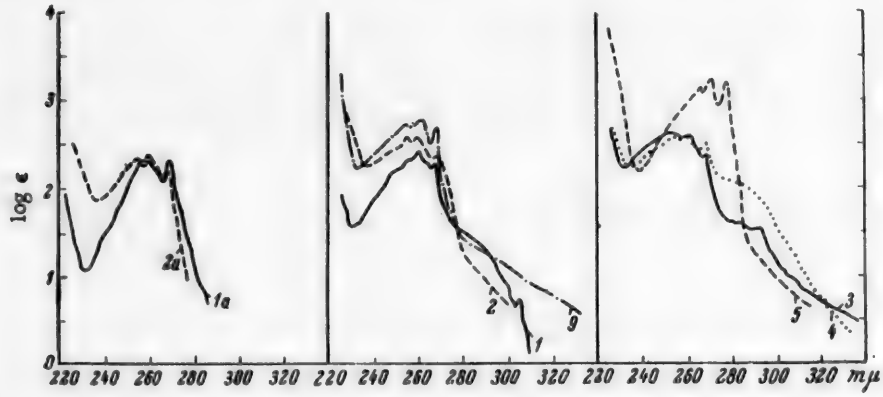

Fig. 1.

1) $C_6H_5CH_2CH=CHCH_3$, 2) $C_6H_5CH_2CH=CHCH_2Cl$, 1a) $C_6H_5CH_3$ [4], 2a) $C_6H_5CH_2CH=CH_2$ [4], 3) $C_6H_5CH_2CH=CHCH_2OH$, 4) $C_6H_5CH_2CH=CHCH_2OCOCH_3$, 5) $C_6H_5CH_2CH=CHCH_2OC_6H_5$, 9) $C_6H_5CH_2CH=CHCH_2C_6H_5$.

Having available a large number of structurally similiar compounds, we attempted to trace the relation between the absorption spectra of these materials and their structures. We used an SF-4 spectrophotometer; isooctane was used as solvent in all cases.

The investigations carried out by Braude et al. [3] showed that compounds of the type $RC_6H_4CHOHCH=CHCH_3$ have absorption spectra similiar to those of the corresponding substituted toluenes, as the isolated double bond does not affect the absorption of the aromatic part of the molecule.

In our case, the spectra of compounds of the type $XC_6H_4CH_2CH=CH-CH_2Y$, given in Figs. 1, 2 and Tables 1, 2, are also very similiar to the absorption spectra of benzene homologs (Fig. 1). Such substituents in the nucleus

as CH_3, halogen or a methoxy group only increase the absorption intensity and displace the curve very slightly toward longer wavelengths and do not essentially change the general appearance of the spectrum. The introduction of a strong chromophore (nitro group) into a molecule greatly affects the character of absorption curves, which under these conditions become analogous to absorption curves of nitrotoluenes (Fig. 3, Table 2).

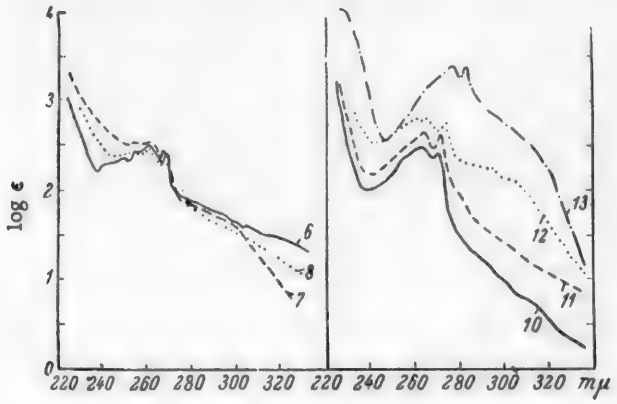

Fig. 2.

6) $C_6H_5CH_2CH = CHCH_2NH_2$, 7) $C_6H_5CH_2CH = CHCH_2N(C_2H_5)_2$,
8) $C_6H_5CH_2CH = CHCH_2N(CH_2)_5$, 10) $o\text{-}CH_3C_6H_4CH_2CH = CHCH_2Cl$,
11) $m\text{-}CH_3C_6H_4CH_2CH = CHCH_2Cl$, 12) $p\text{-}CH_3C_6H_4CH_2CH = CHCH_2Cl$,
13) $p\text{-}CH_3OC_6H_4CH_2CH = CHCH_2Cl$.

Our data on the absorption spectra of arylbutadienes agree quite well with the investigation results of other authors [3, 6]. The absorption curve, characteristic of phenylbutadiene, did not change when a substitutent, which

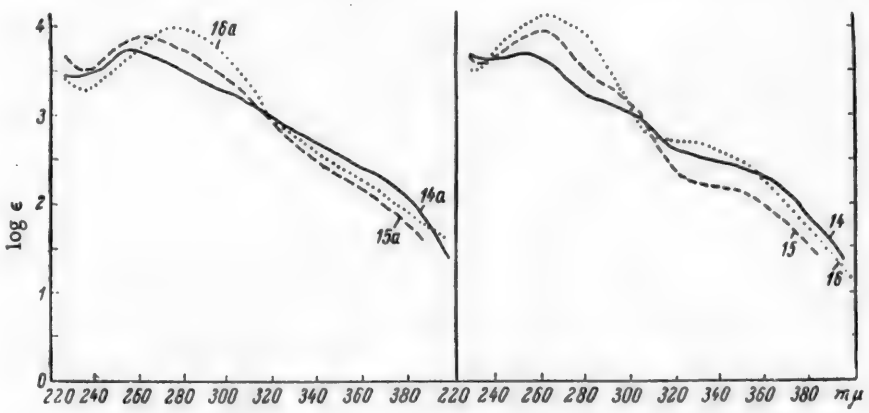

Fig. 3.

14) $o\text{-}NO_2C_6H_4CH_2CH = CHCH_2Cl$, 14a) $o\text{-}NO_2C_6H_4CH_3$ [5], 15) $m\text{-}NO_2C_6H_4CH_2CH = CHCH_2Cl$, 15a) $m\text{-}NO_2C_6H_4CH_3$ [5], 16) $p\text{-}NO_2C_6H_4CH_2CH = CHCH_2Cl$,
16a) $p\text{-}NO_2C_6H_4CH_3$ [5].

was not a strong chromophore, was introduced into the nucleus and the side chain (Figs. 4, 5 and Table 3). The substitution of a double bond by a triple bond (a compound of the type $XC_6H_4CH = CH - C \equiv CH$) hardly affected the absorption spectrum; the absorption and intensity of the main absorption bands of arylbutenynes remained about the same as those of arylbutadienes (Fig. 5 and Table 4).

TABLE 1

No of compound	Formula	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	λ_{max} in mμ (ϵ_{max})					
1	$C_6H_5CH_2CH{=}CHCH_3$	73° (17)	1.5107	0.8852	254 (200)	261 (235)		268 (190)		306 (5)
2	$C_6H_5CH_2CH{=}CHCH_2Cl$	91— 93 (2)	1.5422	1.0547	254 (300)	259 (320)		268 (220)		
3	$C_6H_5CH_2CH{=}CHCH_2OH$	118—119 (3)	1.5423	1.0069	254 (400)	259 (390)		268 (240)	282 (45)	292 (33)
4	$C_6H_5CH_2CH{=}CHCH_2OCOCH_3$	120—121 (3)	1.5178	1.0228	254 (350)	259 (370)		268 (300)	279 (130)	
5	$C_6H_5CH_2CH{=}CHCH_2OC_6H_5$	150 (1.5)	1.5725	1.0479			265 (1200)	271 (1680)	278 (1480)	
6	$C_6H_5CH_2CH{=}CHCH_2NH_2$	83 (3)	1.5403	0.9604	249 (240)	255 (290)	262 (320)	269 (270)		306 (40)
7	$C_6H_5CH_2CH{=}CHCH_2N(C_2H_5)_2$	113 (3)	1.5090	0.9061	254 (300)	259 (290)	261 (300)	268 (220)		
8	$C_6H_5CH_2CH{=}CHCH_2N(CH_2CH_2)_2CH_2$	128 (3)	1.5317	0.9525	254 (280)		262 (300)	268 (220)		
9	$C_6H_5CH_2CH{=}CHCH_2C_6H_5$	M.p. 45—45.5°	—	—	255 (500)		262 (580)	269 (450)		

TABLE 2

No. of compound	Formula	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	λ_{max} in mμ (ϵ_{max})				
10	o-$CH_3C_6H_4CH_2CH{=}CHCH_2Cl$	94—95° (2)	1.5400	1.0434			263 (320)	271 (270)	
11	m-$CH_3C_6H_4CH_2CH{=}CHCH_2Cl$	107—109 (3)	1.5354	1.0320			265 (430)	272 (400)	
12	p-$CH_3C_6H_4CH_2CH{=}CHCH_2Cl$	112—114 (6)	1.5349	1.0227		260 (608)	265 (670)	274 (630)	
13	p-$CH_3OC_6H_4CH_2CH{=}CHCH_2Cl$	124—126 (2)	1.5450	1.0932	228 (11200)			278 (2500)	284 (2440)
14	o-$NO_2C_6H_4CH_2CH{=}CHCH_2Cl$	155—156 (9)	1.5692	1.2226	249 (5000)				
15	m-$NO_2C_6H_4CH_2CH{=}CHCH_2Cl$	174—176 (7)	1.5680	1.2188		258 (8000)			
16	p-$NO_2C_6H_4CH_2CH{=}CHCH_2Cl$	145—146 (2)	1.5740	1.2243			261—264 (12300)		

TABLE 3

No. of compound	Formula	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	λ_{max} in mμ (ϵ_{max})		
17	$C_6H_5CH{=}CH{-}CH{=}CH_2$	65—66° (3)	1.6073	0.9270	233 (6500)	280 (22600)	306 (4500)
18	o-$CH_3C_6H_4CH{=}CH{-}CH{=}CH_2$	86 (7.5)	1.6001	0.9256	236 (7900)	275 (24700)	314 (4100)
19	m-$CH_3C_6H_4CH{=}CH{-}CH{=}CH_2$	86—87 (7)	1.5995	0.9212		277 (24400)	
20	p-$CH_3C_6H_4CH{=}CH{-}CH{=}CH_2$	M.p. 26°	—	—	227 (13000) 235 (8700)	283 (32000)	310 (6900)
21	p-$ClC_6H_4CH{=}CH{-}CH{=}CH_2$	104 (9)	1.6230	1.0728		281—286 (29300)	312 (5800)
22	p-$BrC_6H_4CH{=}CH{-}CH{=}CH_2$	M.p. 29°	—	—		280 283—288 (25200) (25200)	312 (6200)
23	p-$IC_6H_4CH{=}CH{-}CH{=}CH_2$	M.p. 60	—	—		292 (34900)	
24	2,4-$Cl_2C_6H_3CH{=}CH{-}CH{=}CH_2$	M.p. 54	—	—	235 243 (10400) (7500)	275 282 (23400) (23500)	326 (2700)
25	p-$CH_3OC_6H_4CH{=}CH{-}CH{=}CH_2$	M.p. 45	—	—		285—291 (27000)	
26	$C_6H_5CH{=}CH{-}CH{=}CHCH_3$	68—69 (3)	1.6054	0.9312	235 (8320)	282—284 (28800)	
27	$C_6H_5CH{=}CH{-}C(CH_3){=}CHCH_3$	80—82 (2)	1.5900	0.9466	233 (8250)	278—286 (30100)	
28	$C_6H_5CH{=}CH{-}CCl{=}CH_2$	105 (9)	1.6085	0.9356		283 (20350)	
29	$C_6H_5CH{=}C(C_6H_5){-}CH{=}CH_2$	M.p. 55°	—	—		281—285 (27700)	

TABLE 4

No. of compound	Formula	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	λ_{max} in mμ (ϵ_{max})
30	$C_6H_5CH{=}CH{-}C{\equiv}CH$	62° (2)	1.5542	0.9472	276 (15600)
31	$p\text{-}ClC_6H_4CH{=}CH{-}C{\equiv}CH$	88—89 (3)	1.6118	1.1466	280 (17000)
32	$p\text{-}CH_3OC_6H_4CH{=}CH{-}C{\equiv}CH$ . . .	100—105 (3)	1.5965	—	290 (18200)
33	$p\text{-}ClC_6H_4CH{=}C(CH_3)C{\equiv}CH$	90—91 (3)	1.5910	1.0985	282 (16500)

TABLE 5

No. of comp'd	Formula	M.p. (pressure in mm)	λ_{max} in mμ (ϵ_{max})				
34	$o\text{-}NO_2C_6H_4CH{=}CH{-}CH{=}CH_2$ . .	68°		258 (22000)		328 (5150)	
35	$m\text{-}NO_2C_6H_4CH{=}CH{-}CH{=}CH_2$ . .	53		264 (31000)			
36	$p\text{-}NO_2C_6H_4CH{=}CH{-}CH{=}CH_2$ . .	79	233 (14000)		320 (24700)	331 (26000)	
37	$C_6H_5CH{=}CH{-}CH{=}CHC_6H_5$ . . .	156	233 (13000)		315 (47500)	329 (58500)	344 (36800)
38	$p\text{-}CH_3C_6H_4CH{=}CH{-}CH{=}CHC_6H_5$	156	232 (11500)		319 (41200)	332 (51500)	349 (33500)

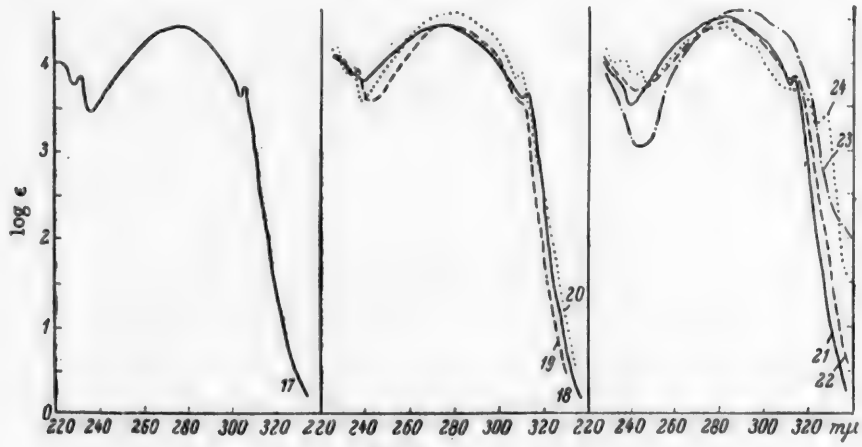

Fig. 4.

17) $C_6H_5CH = CH - CH = CH_2$, 18) $o\text{-}CH_3C_6H_4CH = CH - CH = CH_2$, 19) $m\text{-}CH_3C_6H_4CH = CH - CH = CH_2$, 20) $p\text{-}CH_3C_6H_4CH = CH - CH = CH_2$, 21 $p\text{-}ClC_6H_4CH = CH - CH = CH_2$, 22) $p\text{-}PrC_6H_4CH = CH - CH = CH_2$, 23) $p\text{-}IC_6H_4CH = CH - CH = CH_2$, 24) $2,4\text{-}Cl_2C_6H_3CH = CH - CH = CH_2$.

As in the case of arylbutenes, the introduction of a nitro group into the aromatic nucleus of α-phenylbutadiene sharply changed the character of the absorption spectra (Fig. 6, Table 5). A nitro group in a para-position had an especially strong effect as the conjugation of the whole molecule was thus greatly increased. An aromatic

nucleus, introduced at the end of the side chain also increased the conjugation in the molecule and, therefore, the absorption spectra of compounds $XC_6H_4CH = CH - CH = CHC_6H_5$ are analogous to the p-nitrophenylbutadiene spectrum (Fig. 6 and Table 5).

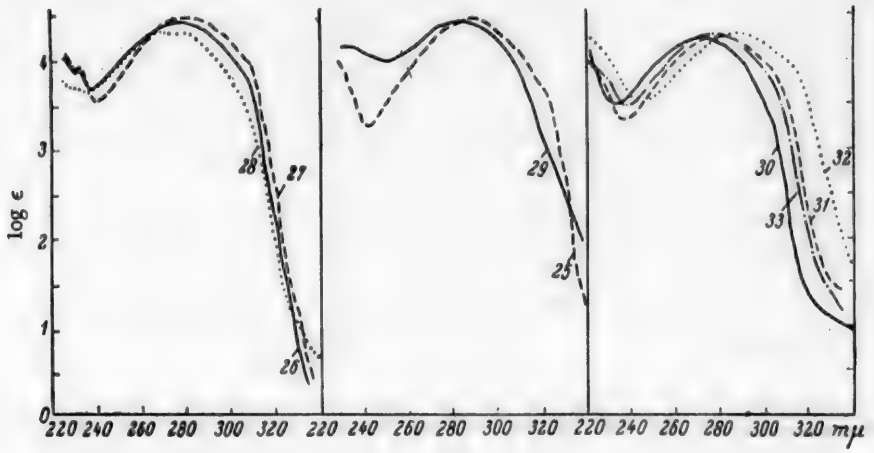

Fig. 5.

25) $p\text{-}CH_3OC_6H_4CH = CH - CH = CH_2$, 26) $C_6H_5CH = CH - CH = CHCH_3$, 27) $C_6H_5CH = CH - C(CH_3) = CHCH_3$, 28) $C_6H_5CH = CH - CCl = CH_2$, 29) $C_6H_5CH = C(C_6H_5) - CH = CH_2$, 30) $C_6H_5CH = CH - C \equiv CH$, 31) $p\text{-}Cl - C_6H_4CH = CH - C \equiv CH$, 32) $p\text{-}CH_3OC_6H_4CH = CH - C \equiv CH$, 33) $p\text{-}ClC_6H_4CH = C(CH_3) - C \equiv CH$.

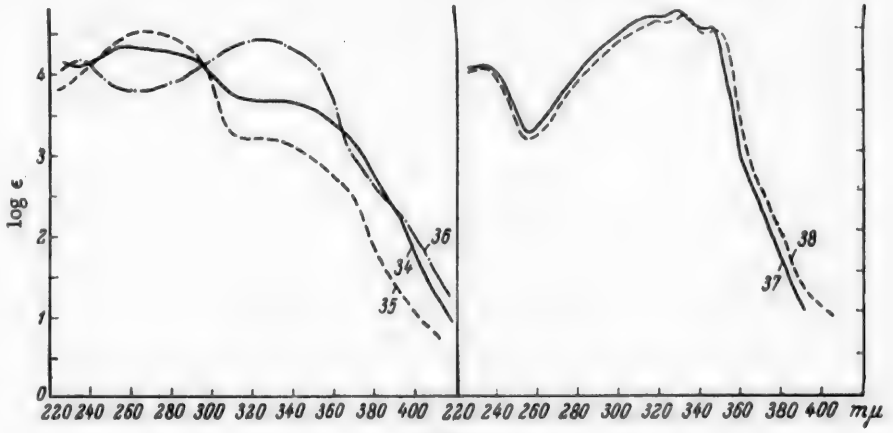

Fig. 6.

34) $o\text{-}NO_2C_6H_4CH = CH - CH = CH_2$, 35) $m\text{-}NO_2C_6H_4CH = CH - CH = CH_2$, 36) $p\text{-}NO_2C_6H_4CH = CH - CH = CH_2$, 37) $C_6H_5CH = CH - CH = CHC_6H_5$, 38) $p\text{-}CH_3C_6H_4CH = CH - CH = CHC_6H_5$.

SUMMARY

1. The absorption spectra of 38 arylbutenes, arylbutadienes and arylbutenynes were plotted.

2. It was shown that substituents in the nucleus that were not strong chromophores, did not affect the character of the spectrum which was determined by the distribution of π-electrons in the molecule.

3. The introduction of a strong chromophore, which resulted in a change in conjugation in the molecule, changed the character of the spectrum.

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HALOARYLATION OF UNSATURATED COMPOUNDS WITH AROMATIC DIAZO COMPOUNDS

VII. REACTIONS WITH ACROLEIN AND CROTONALDEHYDE

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The only example of a reaction of unsaturated aldehydes with aromatic diazonium salts was noted in a paper by Meerwein et al. [1], who found that cinnamaldehyde reacted with p-chlorophenyldiazonium chloride to give α-(p-chlorophenyl)-cinnamaldehyde in 15% yield.

In investigating systematically the reactions of unsaturated compounds with aromatic diazo compounds [2], we studied the reaction of phenyldiazonium chloride and bromide with acrolein (I) and crotonaldehyde (II), which has not been described up to now. In an aqueous acetone solution in the presence of cupric chloride, these aldehydes added a phenyl radical and a halogen atom at the >C=C< double bond. In contrast to cinnamaldehyde, in this case the phenyl radical was added to (I) and (II) in a β-position.

$$\underset{\text{(I)}}{CH_2{=}CH{-}CHO} + C_6H_5N_2X \xrightarrow{CuX_2} \underset{\text{(III) X=Cl, (IV) X=Br}}{C_6H_5CH_2{-}\underset{\displaystyle X}{\underset{|}{C}}H{-}CHO} + N_2$$

$$CH_3{-}CH{=}CH{-}CHO + C_6H_5N_2Cl \xrightarrow{CuCl_2} \underset{\text{(V)}}{C_6H_5{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H{-}\underset{\displaystyle Cl}{\underset{|}{C}}H{-}CHO} + N_2$$

The yields of halophenylation products depended essentially on the pH of the medium and reaction temperature. The best yields (40-53 %) were obtained by treating the aldehydes with neutral solutions of diazonium salts with the addition of calcium hydroxide to the reaction mixture, and maintaining the pH of the medium within the range 5 to 6 at a low temperature (0°-2°). Resinification of the mixture occurred in an acid medium (pH 2) and at 15-20°. Besides α-chloro-β-phenylpropionaldehyde (III) and, correspondingly, α-bromo-β-phenylpropionaldehyde (IV), a series of side products were formed in the reaction (chloro- or bromobenzene, chloro- or bromoacetone, tars). We could not isolate α-chloro-β-phenylbutyraldehyde (V) in a pure form as the elimination of hydrogen chloride occurred during the reaction and a small amount of β-methylcinnamaldehyde was formed.

The structure of compounds (III) and (IV), which are not described in the literature, was proved by oxidizing them with potassium permanganate to α-halo-β-phenylpropionic acids; (V), correspondingly, gave α-chloro-β-phenylbutyric acid on oxidation. The elimination of the hydrogen halide by heating with a 10% solution of sodium hydroxide gave cinnamic (VI) and β-methylcinnamic (VII) acids.

Aldehydes (III) and (IV) are pale yellow liquids, with a strong and characteristic smell reminiscent of the smell of a watermelon; they form monohydrates with water which again lose water at 70-80° or in the presence of a drying agent (P_2O_5).

Treatment of (III) and (V) with an alcohol solution of HCl gave the diethyl acetals of α-chloro-β-phenylpropionaldehyde (VIII) and α-chloro-β-phenylbutyraldehyde (IX), which are stable substances with a pleasant smell. Treatment of (VIII) with sodium ethylate in anhydrous alcohol gave the diethyl acetal of cinnamaldehyde (X).

EXPERIMENTAL

Halophenylation of acrolein. A standard method was used for the reaction in all cases: a solution of the diazonium salt was neutralized with powdered sodium bicarbonate and then gradually added to a suspension of equivalent amounts of cupric chloride and calcium oxide, dispersed in a solution of the aldehyde in acetone. The apparatus in which the reaction was performed was hermetically sealed and the nitrogen evolved passed through a bubble counter. The temperature of the reaction was regulated according to the rate of evolution of nitrogen.

α-Chloro-β-phenylpropionaldehyde (III). Into a three-necked flask, fitted with a stirrer, a thermometer and a dropping funnel, was placed 10 g of cupric chloride, 4 g of calcium oxide and a solution of 22.5 g of acrolein in 200 ml of acetone. With careful external cooling, a neutral solution of 0.4 M of phenyldiazonium chloride in 350 ml of water was gradually added to the mixture at such a rate that nitrogen was evolved at 2-3 bubbles per second (the temperature of the reaction mixture did not exceed 0-2°). After 2 hours the evolution of nitrogen was complete. The reaction mixture was extracted with ether and the ether layer washed with calcium chloride. After distilling off the solvent, the residue was vacuum distilled. We obtained 35.0 g of (III); yield 52.8 %.

B.p. 104-106° (at 12 mm), n_D^{20} 1.5473, d_4^{20} 1.176, MR_D 45.47; calc. 45.41.

Found %: C 64.42, 64.30; H 5.40, 5.32. C_9H_9OCl. Calculated %: C 64.10; H 5.38.

α-Chloro-β-phenylpropionaldehyde hydrate. Into a tared beaker was placed a sample of liquid (III). The preparation was placed under a bell jar, in which the atmosphere was saturated with water vapor at the given temperature, and left until it reached constant weight (4 days). All the aldehyde was converted into a white crystalline hydrate.

Found %: H_2O 8.58. $C_9H_9OCl \cdot H_2O$. Calculated %: H_2O 8.82.

α-Bromo-β-phenylpropionaldehyde (IV). By a method similar to that used for the preparation of (III), we obtained 11.0 g of (IV) from 11.2 g of acrolein in 100 ml of acetone and 0.2 M of a solution of phenyldiazonium bromide in the presence of 5 g of cupric bromide and 2 g of calcium oxide; the yield was 21.5 %.

B. p. 104-105° (at 7 mm), n_D^{20} 1.5673, d_4^{20} 1.425, MR_D 48.88; calc. 47.94.

Found %: C 50.93, 51.00; H 4.15, 4.20; C_9H_9OBr. Calculated %: C 50.72; H 4.25.

In the vacuum distillation we obtained 5 g of bromobenzene with n_D^{20} 1.5604.

α-Bromo-β-phenylpropionaldehyde hydrate. The hydrate of (IV) was formed on standing the aldehyde in air for a short time.

Found %: H_2O 7.54. $C_9H_9OBr \cdot H_2O$. Calculated %: H_2O 7.79.

A sample of the hydrate was placed in a vacuum desiccator over phosphorus pentoxide for two days. The starting aldehyde was obtained as a result.

Cinnamic acid from (III) and (IV). To a suspension of 5 g of (III) in 50 ml of water was gradually added 100 ml of a 4 % solution of potassium permanganate at 10-12°. After separating off the manganese dioxide, the filtrate was evaporated down to 50 ml, 20 ml of a 35 % solution of sodium hydroxide added and the solution boiled under reflux for 30 minutes. After cooling, the solution was acidified and the cinnamic acid precipitated (1 g) had m.p. 133°, after recrystallization from water. Literature data [3]: m.p. 133°. A mixed melting point with the preparation obtained and a sample of cinnamic acid was not depressed. By similar treatment, (VI) was also obtained from (IV).

Diethyl acetal of α-chloro-β-phenylpropionaldehyde (VIII). 20 g of (III) was dissolved in 100 ml of anhydrous alcohol, containing 1.5 % HCl and left for two days at room temperature. The alcohol solution was diluted with water and the precipitated oil extracted with ether. The ether extract was washed with water and dried with calcium chloride. After distilling off the solvent, the residue was vacuum distilled. We obtained 9.52 g of (VIII); yield 67 %.

B.p. 123-125° (at 5 mm), n_D^{20} 1.5010, d_4^{20} 1.064, MR_D 67.22; calc. 66.78.

Found %: C 64.78, 64.71; H 7.73, 7.57; Cl 14.85, 14.92. $C_{13}H_{19}O_2Cl$. Calculated %: C 64.45; H 7.89; Cl 14.61.

Diethyl acetal of cinnamaldehyde (X). 5 g of (VIII) was added dropwise to a solution of sodium ethylate in alcohol, prepared from 0.10 g of sodium in 50 ml of anhydrous alcohol. The mixture was heated at 30-40° for 6 hours. Then 100 ml of water was added to it. The precipitated oil was extracted with ether and the extract washed successively with dilute acid and water and dried. After distilling off the solvent, the residue was vacuum distilled. We obtained 3.77 g of (X); yield 65 %.

B.p. 119-120° (at 5 mm), n_D^{20} 1.5093, d_4^{20} 1.007, MR_D 61.15; calc. 61.45.

According to literature data [4]: for cinnamaldehyde diethyl acetal d^{15} 0.981.

α-Chloro-β-phenylbutyraldehyde (V). From 28 g of crotonaldehyde in 200 ml of acetone and 0.4 M of phenyldiazonium chloride solution in the presence of 10 g of cupric chloride and 4 g of calcium oxide we obtained 29.5 g of (V); yield 40.5 %.

B. p. 93-95° (at 2 mm), n_D^{20} 1.5470, d_4^{20} 1.108, MR_D 52.26; calc. 50.02.

Found %: C 69.52, 69.33; H 6.21, 6.22; Cl 15.24, 15.32. $C_{10}H_{11}OCl$. Calculated %: C 65.76; H 6.06; Cl 19.43.

The substance contained some β-methylcinnamaldehyde, which partly distilled over in the leading fraction.

B. p. 95-100° (at 10 mm), m.p. 93-94° (from petroleum ether), semicarbazone m.p. 205-206°.

Literature data: b.p. 76-77° (at 5 mm) [5], m.p. 95° [6], semicarbazone m.p. 205-206° [7].

β-Methylcinnamic acid from (V). 5 g of (V) was oxidized with potassium permanganate by the method described for (III) and (IV). The β-methylcinnamic acid (VII), obtained after acidification, was isolated as an oil. Probably it was a mixture of cis- and trans-isomers. For the preparation of the trans-isomer, 0.6 g of (VII) was heated for 3 hours with 10.5% sodium hydroxide solution. After acidification, (VII) precipitated with m.p. 97-98°. Literature data: m.p. 97-98° [8].

The diethyl acetal of α-chloro-β-phenylbutyraldehyde (IX). As with (VIII), we obtained 7.6 g of (IX) from 10 g of (IV) in 50 ml of a 2 % solution of HCl in alcohol; yield 59.5 %.

B.p. 125-128.5° (at 6 mm), n_D^{20} 1.5028, d_4^{20} 1.058, MR_D 71.58; calc. 71.40.

Found %: C 65.70, 65.65; H 8.11, 8.15; Cl 13.45, 13.60. $C_{14}H_{21}O_2Cl$. Calculated %: C 65.47; H 8.24; Cl 13.81.

SUMMARY

1. The halophenylation of acrolein and crotonaldehyde is described.

2. We synthesized α-chloro- and α-bromo-β-phenylpropionaldehydes, α-chloro-β-phenylbutyraldehyde and the diethyl acetals of α-chloro-β-phenylpropionaldehyde and α-chloro-β-phenylbutyraldehyde.

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HALOARYLATION OF UNSATURATED COMPOUNDS WITH AROMATIC DIAZO COMPOUNDS

VIII. CHLOROARYLATION OF PHENYL-, VINYL- AND ISOPROPENYLACETYLENE

A. V. Dombrovsky

The reaction of aryldiazonium chlorides with phenylacetylene in an aqueous acetone solution in the presence of cupric chloride ctalyst has not been studied as yet. Meanwhile, this reaction is interesting as it may lead directly to stilbenes. The literature mentions only that in an aqueous alcohol solution phenylacetylene combines with p--nitrodiazobenzene sulfate in the side chain; oxidation occurs simultaneously. As a result of p-nitrophenylhydrazone of phenylglyoxal is formed [1].

The reaction between aryldiazonium chlorides and vinylacetylenes has also not been studied. However, it was reported in a patent [2] that vinylacetylene and certain diazonium salts gave chloroaryl derivatives.

In this work we report the results of studying the reactions of phenylacetylene, vinylacetylene and isopropenylacetylene and aryldiazonium chlorides and some reactions of the chloroaryl derivatives obtained.

We established that under the conditions described by us for divinyl chlorophenylation [3] phenylacetylene reacts at a pH of 4-4.5 with a neutral solution of phenyldiazonium chloride, in 50% excess, to give so-called "α-chlorostilbene". About 30 % of the phenylacetylene remained unchanged.

$$C_6H_5{-}C{\equiv}CH + C_6H_5{-}N_2{-}Cl \rightarrow C_6H_5{-}CCl{=}CH{-}C_6H_5 + N_2$$

The α-chlorostilbene obtained was reduced with zinc in acetic acid to trans-stilbene and treated with potassium hydroxide powder in dioxan to give tolane.

TABLE 1

Chloroarylbutynes $Ar{-}CH_2{-}\underset{\displaystyle R}{\underset{|}{C}}Cl{-}C{\equiv}CH$

Formula	Yield (in %)	No. of acetylene hydrogen atoms found	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated	MR_D exaltation
$C_6H_5CH_2CHCl{-}C{\equiv}CH$	46	1.02	105° (3)	1.5641	1.0788	49.64	47.58	2.06
$p\text{-}ClC_6H_4CH_2CHCl{-}C{\equiv}CH$	23	0.98	107 (2)	1.5737	1.2056	54.46	52.45	2.01
$p\text{-}CH_3OC_6H_4CH_2CHCl{-}C{\equiv}CH$	20	1.12	118—119 (2)	1.5675	1.1263	56.11	53.84	2.27
$C_6H_5{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}Cl{-}C{\equiv}CH$	63	1.05	108 (4)	1.5530	1.0529	54.30	52.20	2.10
$p\text{-}ClC_6H_4{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}Cl{-}C{\equiv}CH$	33	1.03	134—136 (4)	1.5670	1.1698	59.51	57.07	2.44

Phenylacetylene reacted analogously with p-nitrophenyldiazonium chloride.

In this case, crystalline 1-chloro-1-phenyl-2-(p-nitrophenyl)-ethene was formed in 70 % yield (calculated on the reacted phenylacetylene) and after elimination of HCl it gave the known p-nitrotolane.

Vinylacetylene and isopropenylacetylene reacted with aromatic diazonium salts under the same conditions as phenylacetylene, to give 3-chloro-4-arylbutynes-1 (Table 1).

It is interesting to note that the addition of an aryl radical and a chlorine atom occurred preferentially in the positions 3 and 4 to the ethylene bond and not at the triple bond or in positions 1 and 4, as is characteristic of many vinylacetylene reactions. It should also be noted that the chloroarylbutyne yields decreased in the cases where substituents were in the aryl radical. Thus, on reacting p-nitrophenyldiazonium chloride with vinylacetylene, besides small amounts of p-chloronitrobenzene (Sandmeyer reaction products), only a clear, thick resinous mass was formed.

TABLE 2

Arylbutenynes Ar—CH=CR—C≡CH

Formula	Yield (in %)	No. of acetylene hydrogen atoms found	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated	MR_D exaltation
C_6H_5—CH=CH—C≡CH	48	0.92	62° (2)	1.6062	0.9762	45.29	42.25	3.04
p-ClC_6H_4—CH=CH—C≡CH . . .	32	0.88	88—89 (3)	1.6118	1.1466	49.29	45.415	3.83
p-$CH_3OC_6H_4$—CH=CH—C≡CH . .	28	0.82	107 (3)	1.6075	1.0506	52.03	48.51	3.52
C_6H_5—CH=C(CH$_3$)—C≡CH	62	0.90	62 (2)	1.5725	0.9759	47.98	45.13	2.85
p-ClC_6H_4—CH=C(CH$_3$)—C≡CH	34	0.86	90 (3)	1.5910	1.0985	54.36	50.03	4.33

In contrast to vinylacetylene, isopropenylacetylene addition reactions with many addenda occurred mainly at the ethylene bond. This peculiarity explains the higher yields of haloarylation products in reactions with isopropenylacetylene.

The structure of the haloarylacetylenes was established by qualitative and quantitative determination of acetylenic hydrogen. Reduction of 3-chloro-4-phenyl-butyne-1 gave n-butylbenzene.

The elimination of HCl from the chloroarylbutynes obtained was studied. The best results were obtained in reactions carried out by the method we suggested [4] in dioxan with potassium hydroxide powder. On mixing the reagents even at room temperature, a vigorous reaction took place, with the evolution of heat. As a result a series of 4-arylbuten-3-ynes-1 were obtained, whose data are given in Table 2.

$$Ar—CH_2—CCl(R)—C\equiv CH \xrightarrow[\text{dioxan}]{KOH} Ar—CH=C(R)—C\equiv CH + HCl + H_2O$$

R = H, CH_3

The compounds obtained are colorless highly refractive liquids with considerable exhaltation of molecular refraction. They are readily polymerized, especially when heated. This would explain the relatively low yields as on distillation a considerable part is converted into polymeric tars. Quantitative determination of acetylenic hydrogens showed a value close to unity.

EXPERIMENTAL

Chloroarylation of phenylacetylene and the isolation of the reaction products were carried out under the conditions described for the reaction with divinyl [3]. We used 21.4 g of phenylacetylene (b.p. 141-143°, n_D^{20} 1.5496)

in 150 ml of acetone and 150 ml of a solution of phenyldiazonium chloride, prepared from 28 g of aniline and neutralized with sodium carbonate. In addition to 8.5 g of $CuCl_2 \cdot 2H_2O$, 1 g of calcium oxide was added to the mixture. The evolution of nitrogen occurred at 25-30° and pH 5-5.5. From the reaction mixture we isolated 12.5 g of unreacted phenylacetylene and 20 g (46.5 %) of α-chlorostilbene with b.p. 128-135° at 2 mm.

Found %: Cl 16.38, 16.21. $C_{14}H_{11}Cl$. Calculated %: Cl 16.52.

Trans-stilbene. 10 g of the α-chlorostilbene obtained in 50 ml of 80 % acetic acid and 15 g of zinc dust were heated under reflux for 4 hours. After separating off the solid residue, the liquid was diluted with water, the organic part extracted with ether and the extract washed with soda solution and dried with calcium chloride. After removing the solvent, the residue was recrystallized from alcohol. We obtained 7 g (82 %) of colorless, needle-like crystals with m.p. 123°. A mixed melting point was not depressed.

Tolane. A solution of 8 g of α-chlorostilbene in 16 ml of dioxan was added to a boiling mixture of 8.5 g of powdered potassium hydroxide and 20 ml of dioxane. The mixture was stirred for 2 hours. After dilution with water, the thick mass liberated was washed with water. The next day the solid mass was recrystallized from alcohol. The m.p. was 60°; a mixed melting point with authentic tolane was not depressed.

1-Chloro-1-phenyl-2-(p-nitrophenyl)-ethene-2. 21.5 g phenylacetylene in 150 ml of acetone was haloarylated by the method described above with 150 ml of an acid solution of p-nitrophenyldiazonium chloride, prepared by diazotization of 28 g of p-nitroaniline. The evolution of nitrogen occurred at 15-20°. We obtained 30 g of a viscous mass, which was steam distilled to give 6 g (19%) of p-chloronitrobenzene. After recrystallizing the residue from alcohol, we obtained 18.5 g of a yellow crystalline material with m.p. 104°.

Found %: C 64.56, 64.68; H 3.98, 3.92; Cl 13.95, 13.78; N 5.67, 5.56. $C_{14}H_{10}O_2NCl$. Calculated %: C 64.75; H 3.88; N 5.39; Cl 13.66.

p-Nitrotolane. The reaction was carried out by the method described for tolane. From 7.8 g of 1-chloro-1-phenyl-2-(p-nitrophenyl)-ethene-2 we obtained 5.7 g (85 %) of red crystals with m.p. 98° (from alcohol).

Found %: N 6.10, 5.98. $C_{14}H_9O_2N$. Calculated %: N 6.28.

Chloroarylation of vinylacetylene and isopropenylacetylene. The reaction and isolation of the products were carried out by the same method as in the chloroarylation of divinyl [5]. An aqueous solution of aryldiazonium chloride, neutralized with sodium bicarbonate, was gradually added to a solution of the hydrocarbon in acetone, keeping a ratio of 1 : 1 between the solvents. For each 0.1 mole of diazonium salt, 0.025 mole of $CuCl_2 \cdot 2H_2O$ in 10 ml of water and 0.01 mole of calcium oxide were added to the reaction mixture. The yields and constants of the chloroarylbutynes are given in Table 1. The amount of acetylenic hydrogens was determined by a micro method using an ether solution of methylmagnesium iodide [6].

2-Chloro-1-phenylbutyne-3. In the reaction we used 230 ml of a solution of phenyldiazonium chloride (prepared by diazotizing 47 g of aniline) and 36 g of vinylacetylene in 250 ml of acetone. Nitrogen was evolved at -3 to 0° and evolution was complete after 1 hour. We obtained 38 g of a substance and 27.5 g of tar.

Found %: C 72.75, 72.61; H 5.62; 5.56; Cl 21.37; 21.67. $C_{10}H_9Cl$. Calculated %: C 72.95; H 5.51; Cl 21.54.

Hydrogenation of 2-chloro-1-phenylbutyne-3. A solution of 4.1 g of 2-chloro-1-phenylbutyne-2 in 45 ml of alcohol was hydrogenated in a duck* on a mechanical rocker with 4 g of Raney nickel. After 6 days 3328 ml of hydrogen had been absorbed and then absorption ceased. Periodically, small portions of catalyst were introduced into the reaction mixture as the absorption of hydrogen slowed down considerably. In all, 14 g of nickel was introduced. After working up the reaction mixture in the usual way, we obtained about 2.5 g of n-butylbenzene with b.p. 75-76° at 17 mm and n_D^{20} 1.4932. Literature data: b.p. 179-180°, n_D^{20} 1.4936.

2-Chloro-1-(p-chlorophenyl)-butyne-3. The reaction was performed with 170 ml of a solution of diazotized p-chloroaniline (51 g) and 31.2 g of vinylacetylene in 180 ml of acetone. Nitrogen was evolved at -3 to 0°. We obtained 18.5 g of the substance and 42.8 g of tar.

Found %: C 60.35, 60.11; H 4.21, 4.11; Cl 35.81, 35.69. $C_{10}H_8Cl_2$. Calculated %: C 60.33; H 4.05; Cl 35.62.

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* Hydrogenation flask.

2-Chloro-1-(p-methoxyphenyl)-butyne-3. Nitrogen was evolved at 20-23°. From 37 g of diazotized p-anisidine and 23.5 g of vinylacetylene we obtained 11.5 g of the substance and 32 g of tar.

Found %: C 68.01, 68.20; H 5.77, 5.90; Cl 18.70, 18.80. $C_{11}H_{11}OCl$. Calculated %: C 68.34; H 5.74; Cl 18.34.

2-Chloro-2-methyl-1-phenylbutyne-3. In the reaction we used 120 ml of a solution of phenyldiazonium chloride (prepared by diazotizing 28 g of aniline) and 28.5 g of isopropenylacetylene in 140 ml of acetone. Nitrogen was evolved at 14-15°. We obtained 34 g of the substance and 8 g of tar.

Found %: C 74.11, 74.05; H 6.18, 6.18; Cl 19.71, 19.59. $C_{11}H_{11}Cl$. Calculated %: C 73.94; H 6.21; Cl 19.85.

2-Chloro-2-methyl-1-(p-chlorophenyl)-butyne-3 The reaction was performed with 38.3 g of diazotized p-chloroaniline in 150 ml of water and 28.5 g of isopropenylacetylene. Evolution of nitrogen began at 4° and then proceeded vigorously at -4°. We obtained 21 g of the substance and 25 g of tar.

Found %: C 62.21, 62.22; H 4.74, 4.72; Cl 32.91, 33.02. $C_{11}H_{10}Cl_2$. Calculated %: C 61.99; H 4.73; Cl 33.28.

Arylbutenynes. The elimination of hydrogen chloride from the chloroarylbutynes was carried out by the method for the preparation of arylbutadienes [5] with powdered potassium hydroxide in dioxan . 0.4 Mole of KOH in 40 ml of dioxan was used for each 0.1 mole of chloride. The reaction was performed at 50-60°. The arylbutenynes formed white precipitates with alcohol-ammonia solutions of silver nitrate. The acetylenic hydrogens were determined quantitatively by the method in [6]. The yields and constants are given in Table 2.

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THE EFFECT OF THE NATURE OF THE METAL IN METAL DERIVATIVES OF A KETOENOL SYSTEM ON THE DIRECTION OF O- AND C-SUBSTITUTION

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The purpose of this work, which was carried out under the direction of A. N. Nesmeyanov, was to collect additional experimental material on the problem of the effect of the nature of the metal in metal derivatives of tautomeric systems on the direction of substitution reactions. We studied the reactions of the β-naphtholates of Li, Na, K, Tl(I), BrMg and $(CH_3)_4N^+$ with benzyl bromide and Na- and Ag-phenolates with triphenylchloromethane. In addition, the acylation of $(CH_3)_4^+$-, Ag-, Tl(I)-, Li- and Mg-acetoacetic esters was investigated. The results of the main experiments are summarized in the table.

In experiments 1-4, 6 and 7, β-naphthol benzyl ether (O-derivative), 1-benzylnaphthol-2 (C-derivative) and unreacted β-naphthol were isolated from the reaction mixture. The crude β-naphthol benzyl ether contained a considerable amount of an impurity that was difficult to separate and was, in all probability, dibenzylnaphthol. Due to this, the total yields of β-naphthol O- and C-derivatives were not high.

As can be seen in the table, BrMg-β-naphtholate had a greater tendency for benzylation at the C (no O--derivative formed at all) then alkali metal naphtholates. Mg-Acetoacetic ester also formed only a C-derivative with acetyl chloride, while in the acylation of Na-acetoacetic ester with the same acid chloride, besides α-acetylacetoacetic ester (the main reaction product), small amounts of an enol acetate was formed [3, 4].*

It was found earlier [1, 2] that the quaternary ammonium enolates, of known ionic structure, of some ketones, for example β,β-diphenylpropiomesitylene, have a greater tendency for substitution of the O-atom than the corresponding alkali metal and magnesium enolates.

Similiarly to this, with benzyl bromide $(CH_3)_4N^+$-β-naphtholate gave a somewhat greater relative yield of the O-derivative than potassium β-naphtholate (table, experiments 6 and 7). In its turn, the latter was found to be more capable, to a slight extent, than Li and Na naphtholates of forming O-benzylnaphthol (experiments 1-3).

A greater difference in the behavior of ammonium and alkali metal (Li, Na) derivatives was found in benzoylation of the corresponding enolates of acetoacetic ester: $N(CH_3)_4^+$-acetoacetic ester reacted in an alcohol (or ether and alcohol) solution with benzoyl chloride only at the O (experiments 10 and 11). It is known that Na-acetoacetic ester is benzoylated with benzoyl chloride at the carbon in alcohol [5], a mixture of ether and alcohol [6, 7] in ether and other solvents. Only in individual cases were small amounts of enol benzoate isolated [4].

By treating an equimolecular solution of Li-acetoacetic ester and $(CH_3)_4NCl$ with benzoyl chloride in methyl alcohol (the solution was homogeneous before and after reaction) substitution occurred almost exclusively at the O-atom (26 %). In contrast to this, under the same conditions Li-enolate gave C-substituted acetoacetic ester (19 %). No enol benzoate was detected. In both cases a considerable part of the benzoyl chloride (39 and 55 % respectively) was converted into methyl benzoate.

As was noted long ago, Ag salts of tautomeric systems, in particular a ketoenol system (for example Ag--acetylacetone [8]), have a greater tendency for alkylation by haloalkyls at the O, than alkali metal (Na, K) salts. However, as a rule, the reactions of silver and alkali metal salts were carried out under different conditions

* In reacting Na-acetoacetic ester with acetyl chloride in an ether medium (at 0° or boiling) we were usually able to isolate the enol acetate in a relative yield of about 10%.

The Effect of the Nature of the Metal on the Relative* O- and C-derivative Yields

Experiment No.	Metal derivative	Halogen derivative	Solvent and temperature	Derivative yield (in % of theoretical)			Total yield (in % of theoretical O- and C--derivatives**)	Relative yield (in %)	
				O	C	"bis"		O	C
	β-Naphtholates:								
1	Li	$C_6H_5CH_2Br$	Dioxan ; 104-106° (bath temperature)	22	25	Not taken into account	47	47	53
2	Na			23	26		49	48	52
3	K			27	19		46	58	42
4	Tl (I)			27	29		56	48	52
5	BrMg			—	25	51	64	0	100
6	$(CH_3)_4N^+$		Alcohol-benzene (1 : 1); 69-70°(bath temp.)	46	4.3	Not taken into account	50.3	91	9
7	K			39	7.7		46.7	84	16
	Phenolates:								
8	Na	$(C_6H_5)_3CCl$	Ether; 20°	32	38	17	74	44	56
9	Ag			68	2	17	80	84	16
	Enolates of acetoacetic ester:								
10	$(CH_3)_4N^+$	C_6H_5COCl	Alcohol-ether; 0°	21	—	—	21 (68***)	100	0
11	$(CH_3)_4N^+$		Alcohol; −10°	68	—	—	68	100	0
12	Ag		Boiling ether	19	—	—	—	—	—
13	Tl (I)			—	52	Not taken into account	52	0	100
14	Tl (I)		Ether; 0°	—	65		65	0	100
15	Tl (I)	CH_3COCl		17	35	11	58	30	70
16	Mg		Boiling ether	—	65	—	65	0	100

* Relative to the total isomer yield.

** The C-derivative yield was determined taking into account the bis-derivative yield as the latter was formed from the mono-C-derivative.

*** Taking into account the ethyl benzoate formed.

(temperature and solvent). More drastic temperature conditions were used for the less reactive alkali metal salts. This, naturally, made a comparison of the experimental data difficult.

We reacted Na- and Ag-phenolates with triphenylchloromethane under identical conditions (table, experiments 8 and 9) and, in this case, the Ag derivative was found to have a greater tendency for substitution at the O. In exactly the same way, the Ag-enolate of acetoacetic ester had a greater tendency for benzoylation at the O (experiment 12) than the Na-enolate.

The double reactivity of monovalent thallium derivatives has not been studied as yet. It is only known that Tl(I)-acetoacetic ester forms a C-derivative with ethyl iodide [9]. It was found that Tl(I) (table, experiments 4, 13-15) differed little in its effect from Na.

The main results obtained in this work were explained when examining the double reactivity of metal derivatives on a larger scale [10].

EXPERIMENTAL

All the reactions were carried out in absolutely dry solvents.

Na-β-Naphtholate. This was prepared in an atmosphere of dry nitrogen by treating β-naphthol (22 g) with sodium (3.45 g) in boiling xylene (200 ml) [11].

Li-β-Naphtholate. This was prepared as above in a quite pure form.

Found %: Li 5.01, 4.65. $C_{10}H_7OLi$. Calculated %: Li 4.63.

K-β-Naphtholate. This was prepared by the same method in boiling toluene.

Tl(I)-β-Naphtholate. The method described for Tl(I)-α-naphtholate [12] was used for the preparation. The substance was purified by 2 reprecipitations from dioxan with petroleum ether and dried in a vacuum desiccator over P_2O_5 and paraffin. The light yellow, crystalline powder dissolved in benzene and dioxan. It contained $^1/_2$ a molecule of dioxan (sometimes a preparation was obtained with a larger dioxan content).

Found %: Tl 52.48, 52.61. $C_{10}H_7OTl \cdot {}^1/_2\ C_4H_8O_2$. Calculated %: Tl 52.21.

BrMg-β-Naphtholate. This was obtained as a colorless crystalline precipitate on adding a solution of β-naphthol (14.4 g) in ether (40 ml) to ethylmagnesium bromide, prepared from 2.4 g of magnesium and excess ethyl bromide in 60 ml of ether. After purification by precipitation from benzene solution with a mixture of petroleum ether and ether, the naphtholate contained a molecule of ether of crystallization and was readily soluble in benzene and difficultly in ether, acetone and dioxan.

Found %: Br 25.05, 25.12. $C_{10}H_7OMgBr \cdot (C_2H_5)_2O$. Calculated %: Br 24.82.

Na-Phenolate. A mixture of 11.1 g of phenol, 60 ml of dioxan and 3.2 g of sodium was boiled for several hours until the evolution of hydrogen ceased. The solution of the phenolate was filtered, diluted with 150 ml of hot ligroin and cooled and the crystals deposited were filtered off, washed and dried in vacuum (15 mm, 60°, $^1/_2$ hour). We obtained 17 g of sodium phenolate, containing $^1/_2$ a molecule of dioxan of crystallization.

Found %: Na 14.08, 13.96. $C_6H_5ONa \cdot {}^1/_2\ C_4H_8O_2$. Calculated %: Na 14.35.

Ag-Phenolate. In preparing Ag-phenolate we were guided by the paper [13]. A solution of 1 g of phenol and 0.4 g of NaOH in 10 ml of distilled water, freed from CO_2, was gradually added with stirring and cooling in ice to 1.7 g of $AgNO_3$ in 10 ml of water. The white precipitate was filtered, sucked off strongly, washed twice with ice water with careful stirring, spread in a thin layer on a clock glass and dried in a vacuum desiccator over P_2O_5 (15 hours).

Found %: Ag 53.63, 53.48. C_6H_5OAg. Calculated %: Ag 53.56.

Ag-phenolate is a white powder, which is soluble in aqueous ammonia and dilute HNO_3 and insoluble in the usual organic solvents. In light it quickly darkens and decomposes with an explosion on heating.

It is possible to prepare 2-3 times larger amounts of Ag-phenolate with satisfactory results if the precipitate is pressed out between cooled porous plates before placing in the desiccator. The yield was 80-85 %.

Tl(I)-Acetoacetic ester. This was prepared by treating acetoacetic ester (it is better to use a solution in alcohol) with an aqueous solution of TlOH [9]. M.p. 92-93° (from alcohol); according to [9] the m.p. is 91-92°.

Reaction of Na-β-naphtholate with benzyl bromide. 3.76 g of benzyl bromide in 5 ml of dioxan was gradually added over 2 hours 40 minutes in an atmosphere of nitrogen to a solution of 3.32 g of Na-β-naphtholate in 35 ml of dioxan with a bath temperature of 104-106° and heating was continued for a futher 2 hours. On cooling, the reaction mixture was mixed with 0.1 N HCl. The organic material was extracted with ether. Titration of the aqueous layer established that 99 % of the naphtholate had reacted. After evaporating off the ether, the residue, a semi-solid mass, was shaken with 25 ml of an aqueous methanol solution of potassium hydroxide.*

The alkali insoluble material was extracted with 15 ml of a mixture (1 : 1) of benzene and petroleum ether (70-90°). The hydrocarbon extract was washed with 10 ml of alkali and the solvent evaporated off; the residue — the main neutral reaction product — (2.77 g) was recrystallized first from 35 ml of alcohol and then from petroleum ether. We obtained 0.95 g (20 % of theoretical, calculated on the naphtholate taken) of the benzyl ester of β-naphthol with m.p. 97-98°. After a second recrystallization from petroleum ether the material had m.p. 101-102° (according to [15] the m.p. is 99-100°). The picrate had m.p. 122° (according to [16] the m.p. is 123°). An individual substance could not be isolated from the mother liquors.

The alkaline solution was acidified with dilute hydrochloric acid (to congo) and the mixture extracted with ether. The ether was evaporated off and the residue — the main acid reaction product — (1.82 g) was recrystallized from 15 ml of 80% formic acid. We obtained 1.05 g (22 %) of 1-benzylnaphthol-2 with m.p. 109-110°. After a second recrystallization from formic acid the material had m.p. 111-112° (according to [14] the m.p. is 111-112°) and the benzoate had m.p. 96.5-97° (according to [14] the m.p. is 96.5-97.5°). The formic acid mother liquors were evaporated down. To the residue, dissolved in 25 ml of methyl alcohol, was added a 0.01 M mercury acetate in 10 ml of water, acidified with acetic acid. After an hour the precipitate of 1-acetoxymercuronaphthol-2 [17] was filtered off, washed with methyl alcohol** and dried. The weight was 2.1 g. After decomposing the mercury derivative with a boiling mixture of concentrated hydrochloric acid and methyl alcohol (1 : 4), we isolated 0.39 g (14 % of that introduced into the reaction) of β-naphthol with m.p. 118-120°; a mixed melting point with the starting β-naphthol (m.p. 121-121.5°) was not depressed (119.5-121°). The total yield of O- and C-derivatives was 49%, allowing for the β-naphthol recovered.

Note. Under the conditions described, mercury acetate: a) almost qualitatively precipitates β-naphthol in the form of 1-acetoxymercuronaphthol-2; b) does not react with 1-benzylnaphthol-2.

The experiments with Li- and K-β-naphtholates*** were carried out similarly. The results are given in the table (experiments 1 and 3).

Reaction of Tl(I)-β-naphtholate with benzyl bromide. In the reaction 7.80 g of Tl(I)-β-naphtholate and 3.76 g of benzyl bromide were used. To dissolve the naphtholate, containing dioxan of crystallization, 33.2 ml of dioxan was used. The experiment was performed similarly to the previous one; the TlBr formed was removed by filtration. The results are given in the table (experiment 4). The yields of O- and C-derivatives as in the case of the Li- and K-naphtholates, were calculated allowing for the β-naphthol recovered.

Reaction of BrMg-β-naphtholate with benzyl bromide. 6.43 g of naphtholate and 3.76 g of benzyl bromide were used. The reaction was performed as the previous one, but the subsequent heating was continued for 7 hours. 80 % exchange occurred (determined by the increase in the amount of bromide ion). As in the case of the Na--naphtholate, the crude neutral and acid reaction products were isolated. The former was recrystallized from 20 ml of alcohol and then from petroleum ether to give 1.05 g of dibenzylnaphthol with m.p. 98-99° (pure substance). A mixed melting point with the product of benzylating (in boiling dioxan) the BrMg-derivative of 1-benzylnaphthol-2 (m.p. 98°) was not depressed. A mixture with the benzyl ether of β-naphthol melted with depression (70-80°).

Found %: C 88.99, 88.95; H 6.27, 6.40. $C_{24}H_{20}O$. Calculated %: C 88.84; H 6.22

* The alkali solution was prepared by dissolving 250 g of KOH in 250 ml of water and then making up the volume to 1 liter with methyl alcohol [14]. A similar solution of alkali was used in other experiments with phenolates.

** The filtrate and wash solutions did not contain 1-benzylnaphthol.

*** K-β-Naphtholate dissolved incompletely on heating in the amount of dioxan taken, but the Li- and Na-β--naphtholates dissolved without residue.

From the mother liquors we isolated a further 0.25 g of the bis-derivative. The total yield was 1.65 g (51%). Recrystallization of the acid reaction products from 20 ml of formic acid gave 1.20 g (25 %) of 1-benzylnaphthol--2 with m.p. 110.5-111.5°. A mixed melting point with an authentic preparation was not depressed.

Note. a) After boiling a mixture of 2.34 g of the benzyl ether of β-naphthol, 0.85 g of BrMg-β-naphtholate, 1.88 g of benzyl bromide and 20 ml of dioxan for 11.5 hours, 2.18 g (93.1 %) of the benzyl ether of β-naphthol with m.p. 100-101° was recovered from the reaction mixture; b) On boiling (11 hours) in dioxan in the presence of an equimolecular amount of magnesium bromide, the benzyl ether of β-naphthol was not changed (recovered quantitatively).

Reaction of $(CH_3)_4N^+$-β-naphtholate with benzyl bromide. A hot solution of 3.6 g of $(CH_3)_4NCl$ in 20 ml of alcohol was added in an atmosphere of nitrogen to a solution of K-β-naphtholate, prepared from 4.4 g of β--naphthol and 1.17 g of potassium in a mixture of 5 ml of alcohol and 5 ml of benzene, and then 20 ml of benzene was added with cooling. The precipitate of KCl was filtered off, washed with anhydrous alcohol and dry ether and dried, when the weight was 2.15 g (96%). To the solution (without the wash solutions) of ammonium naphtholate obtained (0.0266 mole*) was added 5.1 g of benzyl bromide over 30 minutes in an atmosphere of nitrogen at a bath temperature of 69-70° and the mixture was heated for a further hour and then treated as in the experiment with Na-naphtholate. We obtained 5.30 g of the main neutral fraction, which was recrystallized from petroleum ether to give 2.84 g (46 %) of the benzyl ether of β-naphthol; m.p. 100-101°.

By the usual method we isolated 1.25 g of an alkali-soluble fraction. To remove the β-naphthol, it was dissolved in 10 ml of methyl alcohol and a solution of 3.2 g of mercury acetate in 5 ml of water and 2.5 ml of methyl alcohol, acidified with acetic acid, was added. After 1 hour, the precipitated mercury derivative of naphthol was filtered off, boiled with 5 ml of methyl alcohol, cooled, filtered and washed with 5 ml of cold methyl alcohol; the weight was 1.1 g.

The combined filtrates, containing 1-benzylnaphthol-2, were shaken with 30 ml of a mixture of benzene and ligroin (1 : 1); 50 ml of water was added, the mixture shaken, the upper layer separated and the solvent evaporated off. To remove traces of the mercury derivative, the residue (0.6 g) was dissolved in ether and treated with 3 ml of concentrated hydrochloric acid. After adding water, the solvent was evaporated off from the ether layer to give 0.5 g of material, which was recrystallized from a mixture of petroleum ether and CCl_4. We obtained 0.27 g (4.3 %) of 1-benzylnaphthol-2; m.p. 109.5-111°.

Under similar conditions a reaction was performed between K-β-naphtholate (prepared from 4.4 g of β--naphthol and 1.17 g of potassium in 25 ml of alcohol and 25 ml of benzene) and benzyl bromide. We obtained 2.74 g (39 %) of the benzyl ether of β-naphthol with m.p. 98.5-100° and 0.54 g (7.7 %) of 1-benzylnaphthol with m.p. 106-108°. After recrystallization from formic acid, the latter melted at 110.5-111.5°.

Reaction of Na-phenolate with triphenylchloromethane. The reaction mixture was protected against atmospheric moisture. To 1.00 g of Na-phenolate in 5 ml of ether at 20° a solution of 1.40 g of triphenylchloromethane in 10 ml of ether was added over a period of 20 minutes with stirring. The reaction mixture was stirred for a further hour, left for 15 hours (a sample of the solution gave a negative test for halide with $AgNO_3$) and after adding 20 ml of petroleum ether, extracted (7-8 times) with aqueous-mathanolic alkali in portions of 10-15 ml. The combined alkaline solutions were acidified with dilute hydrochloric acid (to congo), the precipitate was extracted with ether and the ether evaporated off. The p-hydroxytetraphenylmethane obtained was treated with warm water to remove phenol and dried in a vacuum desiccator over sulfuric acid and NaOH. The yield was 0.65 g (38 %), m.p. 280-282°. After recrystallization from glacial acetic acid, 0.63 g of substance with m.p. 282-284° was obtained (according to [18] the m.p. is 284-285°).

The ether and petroleum ether solution of the neutral substances was evaporated in vacuum in the presence o of several drops of alcoholic alkali.** The residue was treated with boiling alcohol and crystallized on cooling. After heating to boiling again, the solid residue, the triphenylmethyl ether of p-hydroxytetraphenylmethane (I)(bis--derivative), was filtered off and washed with hot alcohol to give 0.25 g (17 %) of material with m.p. 196-199°. After recrystallization from petroleum ether the m.p. was 203-205°; the colorless crystals were readily soluble in

* From the difference between the amount of K taken and amount of naphtholate remaining on the filter. The latter was determined by titration of the wash solutions.

** To produce a definitely alkaline medium as in an acid medium, the O-derivative was readily hydrolyzed [19].

benzene, poorly in ether and alcohol and insoluble in water and alcholic alkalis.

Found %: C 91.04, 91.22; H 6.16, 6.09. $C_{44}H_{34}O$. Calculated %: C 91.31; H 5.92.

The combined alcohol solutions were heated to boiling and hot water added with stirring until turbidity appeared. After cooling somewhat, the solution was separated from the slight precipitate and left to cool. The crystals of the phenyl ether of triphenylcarbinol were filtered off, washed with alcohol and dried in a vacuum desiccator over NaOH. The yield was 0.55 g (32 %), m.p. 96-98°. After recrystallization from alcohol, the m.p. was 101-102° (according to [19] the m.p. is 103°, according to [20], 102°).

Note. Under the conditions of the experiment, free phenol does not react with triphenylchloromethane.

Hydrolysis of (I). A mixture of 0.4 g of (I), 5 ml of benzene and 5 ml of concentrated hydrochloric acid was boiled for 2 hours, then added to water and extracted with ether. The ether was evaporated off. By the usual procedure, we isolated 0.15 g (65 %) of p-hydroxytetraphenylmethane with m.p. 280-282° from the residue. A mixed melting point with an authentic sample did not give depression. The alkali insoluble reaction product (0.3 g) was treated with petroleum ether and recrystallized from the same solvent to give 0.02 g of triphenylcarbinol with m.p. 156-158°, which was not depressed (m.p. 157-159°) by admixture with an authentic preparation (m.p. 159-159.5°).

Synthesis of (I). A solution of 0.51 g of p-hydroxytetraphenylmethane in 7 ml of dioxan was boiled for several hours with 0.04 g of sodium. The suspension of the sodium derivative formed was heated with 0.42 g of triphenylchloromethane for several hours and then 0.45 g (52 %) of (I) with m.p. 201.5-203° was isolated by the usual method. A mixed melting point with the analyzed sample was not depressed.

Reaction of Ag-phenolate with triphenylchloromethane. The reaction was carried out similarly to the previous one using 1.25 g of Ag-phenolate (suspension in 5 ml of ether and 0.25 ml of dioxan) and 1.4 g of triphenylchloromethane (solution in 10 ml of ether). At the end of the reaction the precipitate of AgCl was filtered off and washed with ether. The ether solution was treated as above. The results of the experiments are given in the table.

Reaction of $(CH_3)_4N^+$ -acetoacetic ester with benzoyl chloride.* A hot solution of 3.30 g of tetramethylammonium chloride in 20 ml of alcohol was added to a solution of K-acetoacetic ester, prepared from 1.17 g of potassium, 4.00 g of acetoacetic ester and 15 ml of alcohol.

To precipitate the potassium chloride completely, the mixture was cooled in ice and 20 ml of ether added. The solution of ammonium enolate obtained was filtered free from KCl (2.19 g, 98 %), 4.25 g of benzoyl chloride quickly added and the ice bath removed. After 1 hour the mixture was diluted with 30 ml of ether and extracted with a cold 10 % aqueous solution of NaOH. The ether extract was washed with water and dried with $CaCl_2$. The ether was distilled off and the residue vacuum distilled. At 82-87° and 9 mm ethyl benzoate distilled over (2.13 g, 47 %). Then the enol benzoate of acetoacetic ester distilled off: b.p. 140.5-142° at 3 mm (according to [21], b.p. 139° at 1.5 mm). The yield was 1.52 g (21 %).

In agreement with literature data [22], the enol benzoate (1 g) reacted with phenylhydrazine (0.9 g) in ether to give β-benzoylphenylhydrazine (after recrystallization from alcohol 0.6 g, 66 %) with m.p. 167.5-168° (according to [22], m.p. 169°)

The alkaline extract was mixed with ether and acidified with hydrochloric acid (1 : 1) (to congo). The ether layer was separated, washed with sodium bicarbonate solution and dried with $CaCl_2$. The ether was distilled off. The residue (about 1 ml) almost completely distilled at 5-6 mm and a bath temperature of 80° (acetoacetic ester). From the bicarbonate wash solution we isolated 0.6 g of crude benzoic acid.

To the sodium ethylate solution obtained from 2.1 g of sodium and 30 ml of alcohol was added 12 g of $(CH_3)_4NCl$ and the mixture heated to boiling. With cooling (-10°) and stirring 11.7 g of acetoacetic ester was added followed by 12.7 g of benzoyl chloride, after which the mixture was stirred for a further 0.5 hours. On adding ether, as in the previous experiment, we obtained 14.4 g (68 %) of the enol benzoate of acetoacetic ester: b.p. 145° (4.5 mm), n_D^{20} 1.5215, n_D^{40} 1.5115 (by [21] n_D^{40} 1.5110). No C-derivative was found in the alkali extract.

To a suspension of lithium methylate in methyl alcohol (from 0.7 g of lithium and 30 ml of methyl alcohol) was added a solution of 11 g of $(CH_3)_4NCl$ in 20 ml of methyl alcohol and then 13.3 g of acetoacetic ester. 14 g

* Together with L. I. Barsova.

of benzoyl chloride was added dropwise with stirring to the homogeneous solution obtained, at 0°. The reaction mixture was worked up as above.

Distillation of the neutral fraction yielded 5.4 g (39 %) of methyl benzoate with b.p. 70-80° (5.5 mm) and 6.1 g (26 %) of the enol benzoate of acetoacetic ester with b.p. 143-149° (5mm), n_D^{20} 1.5218. From the acid fraction we obtained traces of Cu-α-benzoylacetoacetic ester. On benzoylating 0.1 M of Li-acetoacetic ester under the same conditions (at the end of the reaction a homogeneous solution was formed) we obtained 4.5 g (19%) of α-benzoylacetoacetic ester, b.p. 140-141° (6 mm) together with methyl benzoate (55 %) and 1.4 g of a heterogeneous neutral fraction (b.p. 150-160° at 5.5 mm, n_D^{20} 1.5250); residue 2 g (apparently the bis-derivative).

Reaction of Ag-acetoacetic ester with benzoyl chloride. The Ag-acetoacetic ester was prepared similarly to Ag-phenolate (80 % yield). The light grey powder was readily soluble without turbidity in concentrated ammonia solution and dilute nitric acid; it did not dissolve noticeably in the usual organic solvents.

3.30 g of benzoyl chloride in 5 ml of ether was quickly added dropwise to a suspension of 5.75 g of Ag-acetoacetic ester in 25 ml of ether at 40°. A vigorous reaction occurred. After two hours heating, the silver chloride was filtered off and washed with ether. By the usual method the combined ether solutions yielded 1.07 g (19 %) of the enol benzoate of acetoacetic ester; b.p. 139-141° (3 mm). Like that obtained in previous experiments, the enol benzoate did not dissolve in aqueous sodium hydroxide or give a color with ferric chloride. The residue (2.5 g, apparently the bis-derivative) did not distil at 3 mm without decomposition.

From the alkali soluble fraction we isolated 0.05 g of benzoic acid (bicarbonate extract) and 0.25 g of acetoacetic ester. The residue weighed 0.2 g.

Reaction of Tl(I)-acetoacetic ester with benzoyl chloride. 3.52 g of benzoyl chloride in 7 ml of ether was quickly added to a solution of 8.40 g of Tl(I)-acetoacetic ester in 60 ml of ether at 50°. After heating for 1 hour, 5.75 g of TlCl was formed, i.e. 96 %; by the above method the alkali extract yielded 3.05 g (52 %) of α-benzoylacetoacetic ester; b.p. 144-145° at 6 mm, 125° at 3 mm. From 1 g of the material we obtained 1.05 g (92 %) of the Cu derivative with m.p. 218-219° by shaking with a saturated solution of copper acetate; after recrystallization from benzene the m.p. was 220-221° (according to [23], m.p. 224°).

Distillation of the neutral fraction (1.2 g, probably the bis-derivative) at 200° (bath temperature) and 2 mm yielded 1-2 drops of liquid in all.

Over a period of 45 minutes, 6 g of benzoyl chloride in 10 ml of ether was added to a suspension of 15.1 g of Tl(I)-acetoacetic ester in 40 ml of ether, which was stirred and cooled in ice. The mixture was stirred for 30 minutes and then for 4 hours after the removal of the ice bath. Working up in the usual way yielded an acid fraction, which was directly converted into the Cu derivative (6.60 g, m.p. 220-222°); after recrystallization from benzene the m.p. was 223.5°.

The precipitate of Tl salts, which had been filtered off, was treated with dilute sulfuric acid in the presence of benzene. The benzene was distilled off from the benzene layer and the residue shaken with a solution of copper acetate to give a further 0.66 g of the Cu-derivative. The total yield was 7.26 g (65 %). The neutral fraction (1.8 g) did not contain enol benzoate.

Reaction of Tl(I)-acetoacetic ester with acetyl chloride. Over a period of 45 minutes 4.3 g of acetyl chloride in 10 ml of ether was added to 16.7 g of Tl(I)-acetoacetic ester in 40 ml of ether, which was stirred and cooled in ice, and the mixture was stirred for a further 45 minutes and then worked up as described in the previous experiment. We obtained 3.5 g (35 %) of the Cu-derivative of α-acetylacetoacetic ester with m.p. 150-150.5° (dried in a vacuum desiccator over P_2O_5). After recrystallization from a mixture of benzene and petroleum ether, the material had m.p. 151-151.5° (according to [24], m.p. 152°).

From the neutral fraction we isolated 1.53 g (17 %) of the enol acetate of acetoacetic ester with b.p. 112° at 26 mm, n_D^{20} 1.4442 (according to [22], b.p. 98° at 12 mm; according to [25], b.p. 98° at 9.5 mm, n_D^{20} 1.4447) and 0.6 g (11 %) of diacetylacetoacetic ester with b.p. 117° at 5 mm (according to [21], b.p. 120-122° at 5 mm).

Reaction of Mg-acetoacetic ester with acetyl chloride.* The Mg-acetoacetic ester was prepared by gradually adding acetoacetic ester to an aqueous solution of a mixture of magnesium sulfate, ammonia and ammonium

* Carried out by L. G. Bulavin.

chloride [26]. The white precipitate was filtered off and washed several times with water; after drying in a vacuum desiccator over sulfuric acid and phosphorus pentoxide, it melted with decomposition at 242° (according to [26], m.p. 240° with decomp.).

A mixture of 33.0 g of Mg-acetoacetic ester and 15.7 g of acetyl chloride in 150 ml of ether was boiled for 4.5 hours, while stirred, and then left at room temperature (periodically stirred) for 4 days.

The precipitate was filtered off and washed with absolute ether. The combined ether solutions were extracted with 10 % aqueous sodium hydroxide solution in the cold. The precipitate of magnesium salts, suspended in ether, was gradually added to cold water and the ether layer separated and treated with alkali as described above. The neutral ether solutions did not contain enol acetate.

By the usual method the alkaline solutions yielded 26.1 g of α-acetylacetoacetic ester with b.p. 85-92° at 11 mm; a second distillation gave 22.2 g (65 %) of material with b.p. 86-91.5° at 10 mm (the bulk came over at 91.5°), n_D^{20} 1.4725 (according to [24], b.p. 97-98° at 15 mm, n_D^{20} 1.4729).

SUMMARY

We studied the substitutions at the oxygen and carbon of metal derivatives of phenol, β-naphthol and acetoacetic ester.

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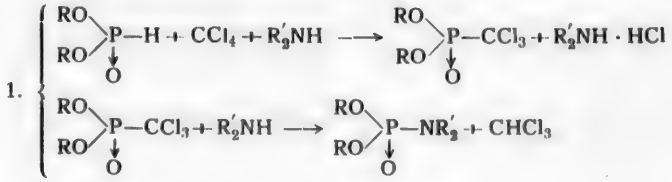
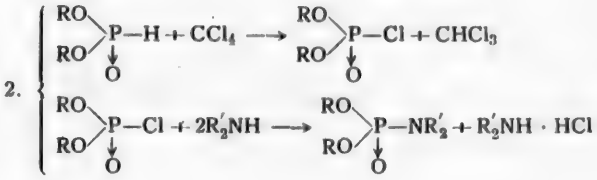
THE REACTIONS OF ALKYL ESTERS OF TRICHLOROMETHYLPHOSPHINIC ACID WITH ALKYLAMINES

Gilm Kamai and F. M. Kharrasova

Atherton, Openshaw and Todd [1] found a convenient method for phosphorylation of amines in the treatment of amines with dialkylphosphites in the presence of carbon tetrachloride. To explain the mechanism of this reaction they proposed the two following schemes



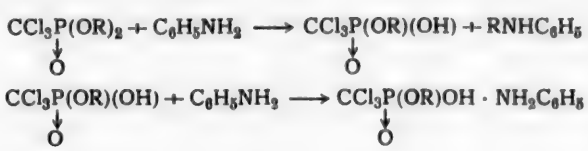


The first scheme shows that the intermediate reaction products are trichloromethylphosphinic esters. However, they could not isolate these esters either from the phosphorylation products or by reacting trialkylphosphites directly with carbon tetrachloride.

Almost simultaneously [2, 3] one of us synthesized various esters of trichloromethylphosphinic acid and, on the basis of preliminary qualitative reactions with certain primary amines, a hypothesis was put forward in favor or the first scheme.

Steinberg [4] showed that no reaction occurred even after 10 minutes when ethyl trichloromethylphosphinate was simply mixed with ammonia.

Yakubovich and Ginsburg [5] and later Kennard and Hamilton [6] proved that trichloromethylphosphinic esters reacted with aniline, not by splitting the Cl_3C-P bond, but by forming the aniline salt of the acid ester of trichloromethylphosphinic acid by the following scheme



The free trichloromethylphosphinic acid reacts with many aromatic amines identically to give a monoamine salt [7].

Exp. No.	Formula	Boiling point, pressure (in mm)	n_D^{20}	d_0^0	d_4^{20}	MR_D** found	MR_D** calc.	P (%) found	P (%) calc.	Yield (in %)
1	$(CH_3)_2NPO(OCH_3)_2$*	72—72.5° (11 mm)	1.4175	1.1535	1.1317	34.06	34.62	20.61	20.23	85
2	$(CH_3)_2NPO(OC_2H_5)_2$*	84 (12 mm)	1.4180	1.0678	1.0469	43.61	43.86	17.05	17.10	66
3	$(CH_3)_2NPO(OC_3H_7\text{-iso})_2$	84—84.5 (12 mm)	1.4160	1.0078	0.9892	53.10	53.09	15.30	14.80	91
4	$(CH_3)_2NPO(OC_3H_7)_2$	125—126 (11 mm)	1.4280	1.0000	0.9826	62.12	62.33	13.71	13.06	84
5	$(C_2H_5)_2NPO(OCH_3)_2$*	82.5—83 (8 mm)	1.4265	1.0885	1.0664	43.57	43.81	17.07	17.10	55
6	$(C_2H_5)_2NPO(OC_2H_5)_2$*	101 (13 mm)	1.4242	1.0297	1.0113	52.79	53.09	14.68	14.80	80
7	$(C_2H_5)_2NPO(OC_3H_7\text{-iso})_2$	115 (20 mm)	1.4205	0.9840	0.9660	62.22	62.33	13.13	13.06	70
8	$(C_2H_5)_2NPO(OC_4H_9)_2$	133.5 (9 mm)	1.4320	0.9814	0.9641	71.37	71.57	11.64	11.70	84

* According to literature data [8], boiling points: 1) 80° at 15 mm; 2) 92° at 13 mm; 5) 100° at 22 mm; 6) 109° at 18 mm.

** The atomic refractions for P and N are respectively 3.75 and 2.502.

In connection with the work mentioned above, we considered it interesting to study, first of all, the reactions of dialkylphosphites with secondary amines in the presence of carbon tetrachloride. By treating dialkylphosphites with dimethyl- and diethylamines in a carbon tetrachloride medium we obtained the corresponding dialkylamidophosphates. Some of their data are given in the table. Four of these dialkylamidophosphates were synthesized for the first time.

The attempt to prepare diphenylamidophosphates by a similiar method was unsuccessful.

The dialkylphosphites reacted extremely vigorously with dialkylamines in the presence of carbon tetrabromide to form also mainly dialkylamidophosphates and dialkylamine hydrobromide. But, in this case the dialkylamidophosphates were contaminated with bromoform and carbon tetrabromide.

We then studied the reaction of trichloromethylphosphinic esters with some secondary amines. The dimethyl ester of trichloromethylphosphinic acid reacted with diethylamine to give the monodiethylamine salt of trichloromethylphosphinic acid. Ethyl and isopropyl esters of trichloromethylphosphinic acid reacted with diethylamine to give ester salts of the composition $CCl_3P(O)(OR)(OH) \cdot NH(C_2H_5)_2$.

Under these conditions, trichloromethylphosphinic esters did not react with diphenylamine.

Thus, according to our experimental results, we can state that trichloromethylphosphinic esters react with both primary and secondary amines not by the first scheme proposed by Todd, Atherton and Openshaw with the formation of aminophosphates and breaking of the Cl_3C-P bond, but with the formation, mainly, of so-called ester salts of trichloromethylphosphinic acid.

All the above indicates that the second mechanism scheme of amine phosphorylation is more accurate [1] as interpreted at the present time [4, 9, 10].

EXPERIMENTAL

Action of dimethylphosphorous acid on dimethylamine in the presence of carbon tetrachloride. A benzene solution of 4.5 g of dimethylamine was added from a dropping funnel to a solution of 5.5 g of dimethylphosphorous acid in 7.52 g of carbon tetrachloride, which was stirred and cooled externally. The formation of dimethylamine hydrochloride as a white precipitate was noticeable after the addition of the first drops. Then the salt was filtered off and washed with ether. After drying over sulfuric acid, 3 g (97%) of dimethylamine hydrochloride with m.p. 169-170° was obtained. The wash ether and filtrate were combined. After distilling off the ether and benzene on a water bath, the residual liquid was vacuum distilled. We obtained a colorless liquid with b.p. 72-72.5° at 11 mm.

According to analysis data, the substance obtained was the dimethylamide of dimethylphosphoric acid.

The other dialkylamides of dialkylphosphoric acids were synthesized by the same method. The results of examining them are given in the table.

Action of dimethyl trichloromethylphosphinate on diethylamine. A solution of 4.5 g of diethylamine in 10 ml of absolute ether was slowly added to 6.8 g of the methyl ester of trichloromethylphosphinic acid (m.p. 36-37°). The reaction proceeded with the separation of a crystalline product. The next day the crystals were filtered off, washed with ether and dried. After two recyrstallizations from acetone-benzine mixtures and drying over phsophorous pentoxide, the crystals melted at 82-82.5°. Determination of the methoxyl groups by the Zeisel method gave a negative result.

Found %: P 11.41; Cl 38.56; N 5.11. $C_5H_{12}O_3NPCl_3$. Calculated %: P 11.37; Cl 39.03; N 5.14.

The acid diethylamine salt of trichloromethylphosphinic acid with the composition $CCl_3P(OH)OH \cdot NH(C_2H_5)_2$ formed white, flaky crystals, which were readily soluble in water, benzene and acetone. The yield was 8.1 g (99.3%).

Action of ethyl trichloromethylphosphinate on diethylamine at an elevated temperature. 11 g of ethyl trichloromethylphosphinate with b.p. 92-93° at 3 mm and 9.48 g of diethylamine were heated in a sealed tube at 40-50° for 6 hours and then at 90-100° for 30 minutes. The tube was cooled and opened and found to be under slight pressure. After removing the volatile products in vacuum, we obtained 14 g of a crystalline material with m.p. 60-61°. The crystals were recrystallized twice from a benzene-benzine mixture and dried over phosphorous pentoxide, when they had m.p. 69.5-70°.

Found %: P 10.11, 10.25; Cl 35.25, 35.38; N 5.0. $C_7H_{17}O_3NPCl_3$. Calculated %: P 10.31; Cl 35.39; N 4.7.

The diethylamine salt of the acid ethyl ester of trichloromethylphosphinic acid formed colorless crystals, which were readily soluble in alcohol, acetone, benzene and water and poorly soluble in ether. The yield was 13.5 g (96.5 %).

By a similar method we obtained the diethylamine salt of the acid isopropyl ester of trichloromethylphosphinic acid with m.p. 100.5-101°. The yield was about 45%.

On reacting the n-propyl and iso- and n-butyl esters of trichloromethylphosphinic acid with dimethyl- and diethylamines, we obtained uncrystallizable, sirupy substances, which were not investigated in detail.

SUMMARY

1. In reacting dialkylphosphites with dimethyl- and diethylamines in the presence of carbon tetrachloride we obtained and studied some new examples of dialkylamidophosphates.

2. It was established that trichloromethylphosphinic esters react with dialkylamines to form, mainly, ester salts and not to break the Cl_3C-P bond and form dialkylamidophosphates.

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A STUDY OF SULFONATION

XLIV. ISOMERIZATION OF BENZENEDISULFONIC ACIDS

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The m- and p-benzenedisulfonic acids formed by benzene sulfonation interconvert at a sufficiently high temperature in a sulfuric acid medium containing water, until a definite equilibrium state is reached between them.

Holleman and Polak [1] found that 6.9 % of the meta-isomer was formed from the para-isomer in 12 hours at 205-210° in 98 % sulfuric acid and that 11 % was formed in 24 hours. In the same way the meta-isomer changes into the para-isomer. Heating the para-isomer under the same conditions but for 168 hours resulted in large amounts of the meta-isomer and the trisulfonic acid.

In trying to achieve an equilibrium between the meta- and para-isomers, Behrend and Mertelsmann [2] used mercury as a catalyst in a sulfuric acid medium at 240-250° and starting with the m-disulfonic acid, obtained a mixture containing 30.8 % of the para-isomer and starting with the p-disulfonic acid, 37 % of the para-isomer.

The purpose of this work was to obtain accurate data on the equilibrium state of the meta- and para-isomers, on the isomerization of o-benzenedisulfonic acid and on the relation of the isomerization rate to sulfuric acid concentration and other conditions for obtaining equilibrium.

EXPERIMENTAL

The isomerization of the sulfonic acids is the result of their hydrolysis and resulfonation. For the hydrolysis products not to accumulate, it is necessary that the rate of hydrolysis should not exceed the rate of resulfonation. It is also necessary to choose the sulfuric acid concentration so that the sulfonation of the isomerizable acids does not proceed further. It is possible that these conditions might be satisfied by a series of sulfuric acid concentrations, however, the isomerization will occur at a maximum rate at a definite sulfuric acid concentration. In order to find this optimal concentration of sulfuric acid at which the hydrolysis products do not accumulate, trisulfonation does not occur and isomerization proceeds at the highest speed, a series of experiments were carried out.

Sulfuric acid was added to a sample of the disulfonic acid in a test tube. The sealed tube was heated in a thermostat, fitted with an electric heater, a contact thermometer and a relay. The temperature was measured with a thermocouple with an accuracy of ± 1°. The reaction products were dissolved in water in a standard flask. The relative rate of m-benzenedisulfonic acid isomerization was determined by the amount of para-isomer formed [3]. By determining the total acidity by a volumetric method, the amount of mono- and trisulfonic acids formed was calculated.

The experimental results are given in Table 1, which shows that at 206°, the isomerization proceeds most rapidly of all in the presence of 90% sulfuric acid. The total acidity of the mixture was unchanged after heating, showing that mono- and trisulfonic acids were absent. At 233° the rate of isomerization also decreased with an increase in the sulfuric acid concentration. In the presence of 100 % sulfuric acid there was trisulfonation, while in 85 % sulfuric acid the rate of hydrolysis was greater than the rate of resulfonation, so that the monosulfonic acid was formed and this we found by the method of Kiprianov and Sych [4]. Thus, the isomerization process proceeded at the optimal rate without the formation of mono- or trisulfonic acids in 90 % sulfuric acid, in which almost all the experiments described below on the isomerization were performed. In 100 % acid it is possible that the isomerization would proceed even more slowly if the water did not separate during the trisulfonation process.

Isomerization of o-benzenedisulfonic acid. In a study of the relative stability of benzenedisulfonic acids to hydrolysis [5], it was established that the ortho-isomer was the most labile isomer; therefore, experiments on the isomerization of o-benzenedisulfonic acid were carried out with short heating. The ortho-isomer content of the sulfonic mixture was determined by precipitating it in the form of the phenylhydrazine salt [3], and the combined ortho- and para-isomers as their 2-naphthylamine salts.

TABLE 1

The Effect of Sulfuric Acid Concentration on the Rate of Isomerization of m-Benzenedisulfonic Acid.

Moles H_2SO_4 taken per mole disulfonic acid	Concentration of sulfuric acid (in %)	Length of heating (in hours)	Found (in % of the total sulfonic acids)			
			mono-acid	meta--acid	para-acid	trisulfonic acid
		At a temperature of		206 ± 1°		
5.93	100	20	0	99.3	0.7	0
5.99	97.2	20	0	99.2	0.8	0
6.02	94.9	20	0	98.3	1.7	0
6.13	92.0	20	0	97.8	2.2	0
6.14	90.1	20	0	97.6	2.4	0
		At a temperature of		233 ± 1°		
6.20	100	24	0	83.8	10.7	5.5
5.99	94.8	24	0	83.7	16.3	0
5.89	90.0	24	0	81.6	18.4	0
6.10	85.6	24	4.1	77.5	18.4	0

In the absence of the ortho-acid, the para-isomer was determined as the benzidine salt.

TABLE 2

Isomerization of o-Benzenedisulfonic Acid at a Temperature of 233 ± 1° in the Presence of 90 % Sulfuric Acid

Moles H_2SO_4 taken per mole disulfonic acid	Length of heating (in hours)	Found (in % of the total sulfonic acids)		
		ortho-isomer	meta-isomer	para-isomer
6.3	0.5	65.9	26.8	7.3
5.9	1	26.5	63.7	9.8
6.3	2.5	6.8	78.9	14.3
6.4	8	0	83.1	16.9

The results of the experiments, given in Table 2, show that the isomerization of o-benzenedisulfonic acid proceeds so rapidly that after 8 hours it could not be found in the sulfonic mixture using phenylhydrazine.

Isomerization of m- and p-benzenedisulfonic acids. In sulfonating barium benzenesulfonate with 98 % sulfuric acid at 183° for 168 hours, Holleman and Polak [1] obtained a mixture of sulfonic acids, consisting of 68.4% of the meta-isomer and 31.6 % of the para-isomer (experiment No. 31). In another experiment (No. 30) they showed that after 48 hours under the same conditions, disulfonation ended with the formation of 14.6 % of the para-isomer. Consequently, after 48 hours the increase in the amount of the para-isomer was the result of isomerization. After heating the meta- and the para-isomers at 180° for 10 hours, there were no signs of hydrolysis in our experiments [5], which contradicts experiments No. 31 of Holleman and Polak. Therefore, we carried out experiments on the isomerization of m- and p-benzenedisulfonic acids at 185° in the presence of 90 % sulfuric acid. The results of the experiments, given in Table 3, show that at 185° the isomerization proceeds extremely slowly. Then we repeated experiment No. 31 of Holleman and Polak, under exactly the conditions they described. By analysis of the sulfonic mixture using the benzidine method, we found only 11.6 % of the para-isomer, i.e. a

slightly larger amount of the p-disulfonic acid then we obtained [6] in the sulfonation of benzene monohydrate at 178°.

TABLE 3

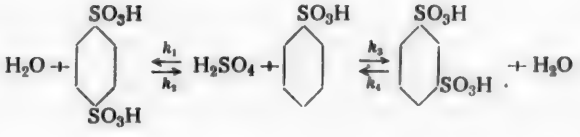
Isomerization of m- and p-Benzenesulfonic Acids in the Presence of 6 ± 0.1 Moles of 90 % Sulfuric Acid per Mole of Disulfonic Acid

Experiment No.	Benzenedisulfonic acid	Temperature	Length of heating (in hours)	Found (in % of the total sulfonic acids)	
				meta-isomer	para-isomer
254	Meta-	185°	204	97.3	2.7
253	Para-	185	204	2.7	97.3
234	Meta-	235	25	81.6	18.4
244		235	50	76.1	23.9
249		235	100	69.3	30.7
261 *		235	200	66.4	33.6
242	Para-	235	20	23.2	76.8
243		235	50	51.7	48.3
248		235	100	61.0	39.0
260 *		235	200	66.2	33.8

Further experiments on the isomerization of m- and p-disulfonic acids were performed at 235 ± 1°. The results of the experiments, also given in Table 3, show that the isomerization of both disulfonic acids proceeds considerably more slowly than the isomerization of o-benzenesulfonic acid. The total acidity of the sulfonic mixtures in experiments No. 248 and 249 decreased by 0.7 % after heating, indicating that small amounts of trisulfonic acid were formed. Therefore, experiments No. 260 and 261 were carried out in the presence of 87 % sulfuric acid, in which the total acidity remained unchanged. The latter experiments showed that after 200 hours at 235° an equilibrium state was practically reached between the isomers, and at this state the mixture contained 66.3 % of m-disulfonic acid and 33.7 % of p-disulfonic acid.

In spite of the fact that the para-isomer is more stable to hydrolysis than the meta-isomer, the labile meta-isomer predominates in the equilibrium mixture. The composition of the mixture, which exists in the dynamic equilibrium and consists of two components, is the result of the different rates of four reactions: the hydrolyses of the sulfonic acids and their formation reactions. In the formation of sulfonic acids, the labile isomers are produced in predominant amounts, but the subsequent processes of their hydrolysis and resulfonation change the original ratios in favor of the isomers more stable to hydrolysis.

In the scheme:



k_1, k_3, k_2 and k_4 are the rates constants of sulfonation and hydrolysis and K_p and K_m are the equilibrium constants between the monosulfonic acid and the corresponding para- and meta-isomers, thus:

$$K_p = \frac{k_1}{k_2} = \frac{[H_2O]\,[\text{para-isomer}]}{[\text{monoacid}]\,[H_2SO_4]} \quad \text{and} \quad K_m = \frac{k_3}{k_4} = \frac{[H_2O]\,[\text{meta-isomer}]}{[\text{monoacid}]\,[H_2SO_4]}$$

Previsouly it was found [6] that the formation of the meta-isomer at 178-206° proceeded at a rate approximately 7.5-9 times greater than the rate of formation of the para-isomer, i.e. $\frac{k_1}{k_3} \simeq \frac{1}{8}$. The rate of hydrolysis of the meta-isomer is approximately 3-4 times greater than the rate of hydrolysis of the para-isomer [5], i.e. $\frac{k_2}{k_4} \simeq \frac{1}{4}$.

The equilibrium constant of the isomerization process in full will be:

$$K = \frac{K_p}{K_m} = \frac{k_1 \cdot k_4}{k_3 \cdot k_2} = \frac{1}{8} \cdot \frac{4}{1} = \frac{[\text{para-isomer}]}{[\text{meta-isomer}]} = \frac{1}{2},$$

which agrees with the composition of the equilibirum found, 33.7 : 66.3. Thus, as a result of the different rates of formation and desulfonation of the isomers, a mixture was obtained in which the predominant isomer is thermodynamically most stable (m-benzenedisulfonic acid) despite the fact that it is most labile kinetically to hydrolysis.

SUMMARY

1. The effect of sulfuric acid concentration was studied on the isomerization rate of m-benzenedisulfonic acid. It was found that at concentrations of 90 to 100% and 206-233° the isomerization rate decreased. The optimal was 90 % (at 206°) or 87 % (at 235°) sulfuric acid.

2. Isomerization of o-benzenedisulfonic acid occurred rapidly at 233° so that after 2.5 hours 7 % remained of that taken.

3. M- and p-benzenedisulfonic acid isomerization proceeded slowly. By heating either the meta- or the para-isomer at 235° for 200 hours in the presence of 87 % sulfuric acid, a state of equilibrium between the isomers was practically achieved. The equilibrium mixture consisted of 66.3 % meta- and 33.7 % para-isomer.

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A STUDY OF SULFONATION

XLV. DETERMINATION OF ISOMERIC CHLOROBENZENESULFONIC ACIDS

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Of the three isomeric chlorobenzenesulfonic acids only p-chlorobenzenesulfonic acid was obtained by the direct sulfonation of chlorobenzene [1]. However, up to now no method has been developed for determining o- or m-chlorobenzenesulfonic acids in the sulfonic mixture formed by the direct sulfonation of chlorobenzene and therefore the absence of o- and m-isomers in the sulfonic mixture is not always proved. Thus, the determination of isomeric chlorobenzenesulfonic acids in sulfonation mixtures is required for the study of chlorobenzene sulfonation.

The meta-isomer in the mixture may be determined by substituting the chlorine in chlorobenzenesulfonic acid with an alkylamino group. In brominating the mixture of isomeric N-alkylanilinsulfonic acids, a sulfonic group in a position ortho or para to the amino group is replaced by bromine. The meta-isomer content may be found by determining the total amount of amine by bromination and the amount of sulfuric acid evolved.

The para-isomer in the sulfonic mixture may be determined by thermal analysis of the chlorobenzenesulfonyl chloride mixture. It is known that the melting point of p-chlorobenzenesulfonyl chloride is 53° [2], that of the ortho-isomer is 28.5° [3] while the meta-isomer does not freeze in a cooling mixture [4]. The m-chlorobenzenesulfonyl chloride, that we synthesized from metanilic acid, crystallized when cooled to -25° and after purification was obtained with an m.p. of 26.3°. According to our determinations, the melting point of o-chlorobenzensulfonyl chloride was 26.2°. The fusion curve we found for ternary mixtures of sulfonyl chlorides makes it possible to determine the para-isomer in the mixture.

EXPERIMENTAL

Substitution of chlorine. Experiments on the substitution of chlorine in chlorobenzenesulfonic acids were performed by heating the compounds in sealed tubes with excess of different amines, as aqueous solutions, with cuprous chloride as a catalyst. The results of the experiments, given in Table 1, show that under the given conditions, the reaction proceeds satisfactorily only with methylamine, which was used in all the following experiments.

In experiments with subsequent bromination to determine m-chlorobenzenesulfonic acid, artificial mixtures were prepared from the pure sodium salts of the isomeric chlorobenzenesulfonic acids. The mixtures were heated for 15 hours at 180° with 10 moles of 38-40 % methylamine solution and 0.1 mole of cuprous chloride per mole of sulfonic acid salt. The product was diluted with water, made alkaline with sodium carbonate and the excess amine removed by boiling. The acidified solution was then made up to the mark in a standard flask, then an aliquot portion was treated with hydrogen sulfide to remove copper and the total content of the three isomers determined bromatometrically. In another portion, after bromination and separation of the tribromo derivative, the sulfuric acid was determined gravimetrically to calculate the total of the ortho- and para-isomers. Experiments with artificial mixtures gave good results, as is shown in Table 2.

Thermal analysis. Experiments showed that a characteristic of the system of isomeric sulfonyl chlorides was the very low rate of crystallization of its components, especially the ortho- and meta-isomers and also binary and ternary mixtures. Therefore it was not possible to apply the usual method of "cooling curves" to the given mixtures as the maximal temperature of crystallization depended very strongly on the degree of supercooling and the rate of heat emission, which lead to poorly reproducible results. Therefore we used the method in which the tem-

• Due to an error in pagination which was discovered too late to remedy, there is a ten-page jump between the last page of the previous article and the first page of this article.

perature of disappearance of the last crystals of the solid phase is determined and also that at which the melt changes from turbid to clear on heating. Then on slowly lowering the temperature with continuous stirring and the periodic addition of seeds, the temperature was determined at which turbidity first appeared. Sometimes the observation was repeated several times until the difference between the points of appearance and disappearance of the solid phase did not exceed 0.1°.

TABLE 1

Substitution of Chlorine by an Alkylamino Group in Chlorobenzenesulfonic Acids (10 moles of amine and 0.1 mole of Cu_2Cl_2 per mole of sulfonic acid)

Taken			Length of heating (in hours)	Temperature	Chlorine substituted (in %)
sodium salt of chlorobenzenesulfonic acid	amine	concentration of amine (in %)			
Para-	Diethylamine	90	20	200°	10.9
	Dimethylamine. . .	33	20	202	59.5
	Piperidine	68	20	209	79.1
	Methylamine	40	20	187	102.0
Meta-	Methylamine	40	20	187	99.9
	Methylamine	40	10	187	98.7
Ortho-	Methylamine	40	20	187	96.4

TABLE 2

Determination of m-Chlorobenzenesulfonic Acid in Artificial Mixtures

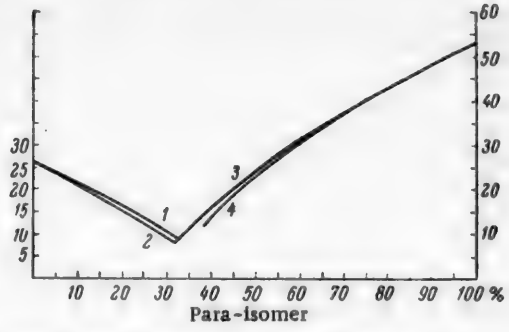
Chlorobenzenesulfonates taken (in % of the total)			Found		
			chlorine substituted (in %)	sulfonates	
ortho-	para-	meta-		total of ortho- and para-	meta-
21.7	31.2	47.1	100.2	53.2	47.0
36.5	40.5	23.0	100.0	76.8	23.2
65.7	14.7	19.6	100.3	80.4	19.9

An advantage of the system studied is practically complete correspondence of the arms of the fusion curves of mixtures of para — ortho and para — meta, beginning from the pure para-isomer down to the eutectic point of the para- and ortho-isomers. The melting point curves of ternary mixtures of para- with the ortho- and meta--isomers passed slightly lower than the two binary curves para — ortho and para — meta, when plotted on a graph. The results of experiments to determine the melting points of binary and ternary mixtures, given in Table 3, make it possible to construct the fusion curves, illustrated in the figure. The curves show that with a para-isomer content from 100 to 60 %, or better from 100 to 70 %, it is possible to determine the para-isomer in the ternary mixture with an accuracy in the region of ± 0.5 %, by measuring the temperature of fusion and crystallization. In the case of mixtures with a low para-isomer content, it is necessary to add a known amount of the pure para-chloride to the mixture.

The ortho — para-isomer system gives a eutectic at 9°, corresponding to 72.5 % of the ortho isomer. The eutectic point of the meta — para-isomer system is at 8° and corresponds to 71.5 % of the para-isomer.

Apparatus. The sample examined was placed in a vessel with double walls and a ring stirrer. The measuring apparatus consisted of a sensitive head — a thermocolumn of four series-connected copper — constantin thermocouples and a constant current potentiometer. The thermocolumn was made up as a bundle of wires, enclosed in a capillary, cemented with carbinol glue. The ends of the bundle were hermetically sealed by dipping in molten polycaprolactam. The temperature of the "cold junctions" was kept at 0°. The thermocolumn was graduated

against a normal thermometer. The reproducibility of the diagram points for the working part of the curve was ± 0.2° and 0.4 %.



Fusion curves of binary and ternary systems.
1) p- + o-, 2) p- + m-, 3) p + o- and p- + m-, 4) o- + m- (1 : 1) + p-

The three isomeric chlorobenzenesulfonic acids were prepared from sulfanilic, metanilic and orthanilic acids via diazotization and the Sandmeyer reaction. The sulfonic acid salts were converted into acid chlorides, which were distilled in vacuum and recrystallized from petroleum ether. The m-chlorobenzenesulfonyl chloride, which was previously known as an oil, crystallized on cooling to -25°. On introducing a seed, crystallization proceeded readily and at higher temperatures.

The melting point of o-chlorobenzenesulfonyl chloride found by us (26.2°) is lower than that given by Bahlmann (28.5°) [3]. Many recrystallizations from petroleum ether and mixtures of it with diethyl ether failed to raise the melting point. Then the chloride was hydrolized and from the sulfonic acid we prepared the m-toluidine and m-4--xylidine salts, which were recrystallized many times to constant melting points (249-250° and 228.5-229.2°). The chloride obtained from these via the sodium salts again melted at 26.2°. Finally, fractional crystallization of the chloride gave a series of fractions, each of which melted at 26.2°.

TABLE 3

Melting Points of Binary and Ternary Mixtures of o-, m- and p-Chlorobenzenesulfonyl Chlorides

Binary mixture						Ternary mixture			
ortho-	para-	temp. of disappearance of solid phase	meta-	para-	temp. of disappearance of solid phase	ortho-	meta-	para-	temp. of disappearance of solid phase
7.3	92.7	49.5°	0	100	52.8°	0	0	100	52.8°
17.5	82.5	44.1	3.9	96.1	51.1	11.3	11.3	77.4	41.6
26.8	73.2	39.0	31.2	68.8	36.1	12.2	12.2	75.6	40.4
30.8	69.2	36.0	40.2	59.8	30.9	20.3	20.3	59.4	30.2
36.2	63.8	33.1	44.4	55.6	28.0	25.8	25.8	48.4	22.0
42.5	57.3	29.1	52.5	47.5	22.1	31.1	31.1	37.8	11.8
47.0	53.0	26.0	63.4	36.6	12.5				
51.3	48.7	22.8	71.0	29.0	9.7				
63.0	37.0	12.4	81.6	18.4	16.3				
67.9	32.1	9.2	91.5	8.5	21.8				
72.1	27.9	11.9	100	0	26.3				
78.3	21.7	15.3							
87.6	12.4	20.0							
92.8	7.2	22.6							
97.2	2.8	24.6							
100.0	0	26.2							

In the same way the meta-isomer was purified. The meta-chloride obtained has m.p. 26.3°. The boiling point of the meta-chloride was 128° at 8 mm, of the ortho-chloride 142° at 9 mm and of the para-chloride 165° at 35 mm.

SUMMARY

The melting point curves were found for the binary systems of o-chlorobenzenesulfonyl chloride with the para-isomer and the meta-isomer with the para-isomer.

A study of the melting points of the ternary mixtures of o-, p- and m-chlorobenzenesulfonyl chlorides made it possible to determine the amount of the para-isomer in the ternary mixture by thermal analysis.

It was shown that chlorine was quantitatively substituted by the methylamino group in chlorobenzenesulfonic acids. The meta-isomer was determined in a mixture of chlorobenzenesulfonic acids by brominating the amino-substituted acid.

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OXAMIC ESTERS OF THE AROMATIC SERIES

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Up to now, the only oxamic ester of the aromatic series known was the phenyl ester and this was prepared by Wallach and Liebmann [1] in very low yield by reacting phenol with the mixture of crude reaction products from phosphorus pentachloride and ethyl oxamate (oxamethane). Wallach and Liebmann presumed that by reacting phosphorus pentachloride with oxamethane the corresponding "amide chloride" would be formed, and this would react with phenols and alcohols by scheme (I).

$$C_2H_5OCOCCl_2NH_2 + ROH \longrightarrow C_2H_5Cl + HCl + ROCOCONH_2 \qquad (I)$$

Wallach could not explain this strange direction of the reaction.

It was shown recently that "amide chlorides" of structure $RCCl_2NH_2$ do not exist or in any case have not yet been obtained and that actually the reaction products of phosphorus pentachloride and oxamic esters are amides of dichloroalkoxyacetic acids and trichlorophosphazodichloroalkoxyacetyls [2]. It was also shown that scheme (I) is inaccurate and that the formation of oxamic esters is actually explained by scheme (II).

$$NH_2COCCl_2OR + R'OH \longrightarrow NH_2COC(OR)(OR')Cl \longrightarrow \begin{cases} RCl + NH_2COCOOR' & (IIA) \\ R'Cl + NH_2COCOOR & (IIB) \end{cases}$$

The very low yields of oxamic esters obtained by Wallach and Liebmann may be explained by the very small amount of dichloroethoxyacetamide in the mixture of crude reaction products of phosphorus pentachloride and oxamethane. As dichloroalkoxyacetamides are now readily available substances [2], it seemed interesting to study reaction (II) more thoroughly.

The application of reaction (II) for preparing esters of oxamic acid and saturated acyclic alcohols did not have any special value as these esters may be prepared by simpler methods [3]. However, the situation is different for oxamic esters of the aromatic series. Up to now, no general method for preparing these esters was known and thus only the phenyl ester had been prepared [1]. It is very obvious that reaction (II) is especially suitable for the preparation, in particular, of aromatic esters, as when treated with aliphatic alcohols the intermediate product may decompose in two directions with the formation either of a new ester (IIA) or of the ester from which the initial dichloroalkoxyacetamide was prepared (see IIB). However, with phenols the formation of halobenzenes is very improbable and therefore the undesirable reaction forming the initial oxamic esters cannot occur. The experiments fully confirmed these hypotheses. In fact, treatment of dichloroalkoxyacetamides with phenol gave a series of aromatic oxamic esters in good yields. The reaction proceeded somewhat more readily with dichloromethoxyacetamide than with dichloroethoxyacetamide, which was quite understandable, as methyl chloride, as a rule, splits off more readily than ethyl chloride. However, it was more convenient to use the more accessible dichloroethoxyacetamide for practical purposes.

Oxamic esters of the aromatic series are colorless, crystalline substances, without smell, stable in the absence of moisture and melt without decomposition above 100°.

As with aliphatic oxamic esters, they are extremely readily hydrolyzed by alkali. Hydrolysis, although somewhat slower than that of aliphatic esters, proceeded at room temperature and at such a rate that they could be

titrated with a 0.2 N solution of sodium hydroxide in aqueous alcohol in the presence of phenolphthalein. See the experimental part of the other properties of oxamic esters.

EXPERIMENTAL

General method of preparing aryl esters of oxamic acid. A mixture of 0.06 mole of dry, freshly prepared dichloroethoxyacetamide and 0.06 mole of the appropriate phenol was heated with continuous stirring in a round-bottomed flask, fitted with a reflux condenser protected with a Tishchenko bottle with sulfuric acid. The temperature was quickly raised (the bulb of the thermometer must be submerged in the reaction mixture) until the evolution of gases began (60-80°). Usually the reaction lasted 10-20 minutes. At the end of the reaction the temperature was raised almost to the melting point of the oxamic ester obtained. On cooling, the liquid and usually colored, reaction product crystallized completely. For purification, the crude reaction products were washed with appropriate solvents and recrystallized. The yields of "crude" oxamic esters were close to theoretical, but purification resulted in considerable losses as in some cases the impurities were removed with great difficulty. In addition, the purification was made more difficult by the ease of hydrolysis of the oxamic esters (see below).

For the phenyl ester of oxamic acid several experiments were performed in which the ethyl chloride and hydrogen chloride evolved were trapped and 90.0 % of ethyl chloride and 91.0 % of hydrogen chloride were obtained.

Purification of crude oxamic esters. Before each wash, the substance was carefully powdered. The substance was washed at room temperature with dry solvents under the usual conditions. After washing with water, the substance had to be carefully dried in vacuum at a temperature no higher than 25°, especially if it was to be recrystallized subsequently. Only completely anhydrous solvents had to be used for recrystallization as the oxamic esters were very readily hydrolyzed on boiling in solutions containing only small amounts of water. The amount of solvent is given for 0.06 mole of starting materials.

Esters of Oxamic Acid of the Type $NH_2COCOOAr$, Prepared by Scheme (II A)

Ar	Yield (in %)	Melting point	N content (in %)		Solubility						
			found	calculated	water	alcohol	acetone	ether	benzene	carbon tetrachloride	petroleum ether
C_6H_5	78.0	131—132°	8.52 8.54	8.49	—	+	+ +	=	—	=	=
o-$CH_3C_6H_4$ . . .	45.0	111—112	8.04	7.82	—	+	+ +	=	—	—	=
m-$CH_3C_6H_4$ . . .	25.0	100—101	7.92	7.82	—	+	+ +	=	—	—	=
p-$CH_3C_6H_4$ . . .	65.0	125—126	7.85	7.82	—	+	+ +	=	—	—	—
p-ClC_6H_4	50.0	174—176	6.91	7.02	—	—	—	=	=	=	=
p-$NO_2C_6H_4$ . . .	44.0	146—147	13.45	13.33	—	—	—	=	=	=	=
α-$C_{10}H_7$	21.0	165—166	6.69	6.51	=	—	+	—	—	=	=
β-$C_{10}H_7$	40.0	170—171	6.62	6.51	=	—	—	=	=	=	=

Note. Symbol meaning: (=) insoluble at boiling point, (—) insoluble at 20°, soluble at boiling point; (+) soluble at 20°, $\left(\begin{matrix}+\\+\end{matrix}\right)$ very readily soluble at 20°.

Phenyl ester. This was washed with ether (4 × 5 ml) and water (3 × 10 ml) and dried in vacuum. It was crystallized from 30 ml of benzene and washed with ether (2 × 5 ml). The colorless, thin needles were up to 10 mm long.

o-Tolyl ester. This was washed with ether (2 × 10 ml), recrystallized from 65 ml of benzene with activated charcoal, washed with benzene (2 × 5 ml) and water (2 × 10 ml), dried in vacuum and recrystallized from 50 ml of benzene (heating the solution for the shortest possible time). The substance formed tufts of thin needles, similar to snow flakes.

m-Tolyl ester. To the uncrystallized crude product was added 20 ml of ether. After 4 hours, the material was sucked off and washed with ether (3 × 10 ml). It was recrystallized from 50 ml of benzene with activated charcoal, washed with water (10 ml) and dried in vacuum. It was then recrystallized from 300 ml of a mixture of benzene and petroleum ether (1 : 1). It formed long, thin needles.

p-Tolyl ester. This was washed with ether (2 × 10 ml) and water (10 ml), dried in vacuum and recrystallized from 80 ml of benzene. It formed colorless, clear needles.

p-Chlorophenyl ester. This was recrystallized from 160 ml of alcohol and washed with ether (2 × 10 ml).

p-Nitrophenyl ester. This substance was recrystallized from 50 ml of methanol and washed with ether (2 × × 5 ml). It formed fine, colorless prisms.

α-Naphthyl ester. The material was washed with alcohol (5 ml) and recrystallized from 65 ml of alcohol with activated charcoal. It formed tufts of colorless needles.

β-Naphthyl ester. This was washed with alcohol (2 × 5 ml) and recrystallized from 100 ml of alcohol with activated charcoal. The thin, colorless needles were up to 20 mm long.

SUMMARY

It was shown that treatment of dichloroalkoxyacetamides with phenols gave aromatic oxamic esters and that this reaction is a general one for preparing these esters.

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SALTS OF ARYLSULFONAMIDOPHOSPHORYL DICHLORIDES

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Phenylsulfonamidophosphoryl dichloride reacts with aniline in an ether solution to form a compound with the composition $C_6H_5SO_2NHPOCl_2 \cdot C_6H_5NH_2$, which precipitates from the solution in the form of a crystalline deposit and does not react further with aniline at room temperature. The substance may be recrystallized from chloroform without decomposition, it dissolves readily in water and is hydrolyzed when the aqueous solution is heated. The properties of this compound (relatively stable and soluble in water) indicated that it was a salt with the composition $[C_6H_5SO_2NPOCl_2]^-[C_6H_5NH_3]^+$. It was therefore decided to examine whether arylsulfonamidophosphoryl dichlorides would also form salts with alkali metals. This hypothesis was fully confirmed. In fact, potassium carbonate or sodium carbonate treatment of arylsulfonamidophosphoryl dichloride or trichlorophosphazosulfonaryls gave remarkably stable salts, that crystallized well, in good yields by the following schemes:

$$2ArSO_2NHPOCl_2 + K_2CO_3 \rightarrow 2[ArSO_2NPOCl_2]^-K^+ + CO_2$$

$$ArSO_2N{=}PCl_3 + K_2CO_3 \rightarrow K^+[ArSO_2NPOCl_2]^- + CO_2 + KCl.$$

A very convenient method for preparing the potassium salt was to introduce the arylsulfonamidophosphoryl dichlorides into a cold saturated solution of potassium carbonate. The reaction products thus formed precipitated from the solution in the form of crystalline deposits. By this method we prepared the potassium salts of phenyl-, p-tolyl-, o-, m- and p-nitrophenyl- and p-chlorophenylsulfonamidophosphoryl dichlorides. These salts were colorless crystalline substances which dissolved readily in water, less readily in methyl and ethyl alcohols and were insoluble in benzene and ether. They hydrolyzed very slowly in neutral or weakly alkaline aqueous solutions at room temperature. When heated carefully, without bringing the solutions to the boil, the potassium salts of arylsulfonamidophosphoryl chlorides may be recrystallized from aqueous methyl or ethyl alcohols and some even from water. When boiled in aqueous solutions, they rapidly hydrolyzed.

Potassium salts of arylsulfonamidophosphoryl dichlorides reacted readily with sodium methylate to form dimethyl esters of arylsulfonamidophosphoric acids by the scheme

$$ArSO_2NKPOCl_2 + 2CH_3ONa \rightarrow ArSO_2NKPO(OCH_3)_2 \xrightarrow{+HCl} ArSO_2NHPO(OCH_3)_2,$$

which quite definitely proved their structure.

The facility with which salts of arylsulfonamidophosphoryl dichlorides formed and their stability to hydrolysis explain why the hydrolysis of trichlorophosphazosulfonaryls with a potassium carbonate solution (see above) stopped at the formation of the potassium salt of phenylsulfonamidophosphoric acid, while at the same time this compound was hydrolyzed with water very readily to break the P — N bond [1]. This also explains why the first stage of trichlorophosphazosulfone-α- and β-naphthyl hydrolysis with a sodium hydroxide solution proceeded 7 times more rapidly than the second stage [2].

In reacting arylsulfonamidophosphoryl dichlorides with metal alcoholates or phenolates, salts are undoubtedly formed first. This is confirmed by existing observations. Thus, for example, in reacting sodium phenolate with o-tolylsulfonamidophosphoryl dichlorides the reaction mixture, consisting of sodium phenolate powder, finely ground dichloride and benzene, first became a porous, spongelike mass when shaken, then started to evolve heat and the spongelike mass became a solution [3]. Apparently, the formation of the porous, spongelike mass corresponded to the stage of sodium salt formation.

It is also understandable why 3 moles of sodium alcoholate must be taken per mole of arylsulfonamidophosphoryl dichloride to obtain good yields of diesters [4].

It was noted quite a while ago that arylsulfonamidophosphoryl dichlorides reacted much less vigorously with sodium alcoholates than trichlorophosphazosulfonaryls [4]. This is also explained by the fact that the dichlorides first form chemically less active salts that are often difficultly soluble.

Most of the arylsulfonamidophosphoryl dichlorides, whose salts are described in this paper, were prepared previously [1, 5]. Trichlorophosphazosulfone-p-chlorophenyl and p-chlorophenylsulfonamidophosphoryl dichloride and the methyl esters corresponding to them were prepared for the first time.

EXPERIMENTAL

The potassium salts of arylsulfonamidophosphoryl chlorides. 0.01 mole of finely powdered arylsulfonamidophsophoryl chloride was introduced in small portions into a saturated aqueous solution of 5 g of potassium carbonate, which was vigorously stirred at room temperature. The reaction occurred in 10-15 minutes without any noticeable increase in temperature. The reaction product was sucked off, washed with a small amount of ice water and alcohol and dried. During recrystallization, the solutions were not heated above 70-80°. The yields were determined for the unpurified products. The acid equivalent after hydrolysis was determined by gently heating the product with a solution of alkali. Phenolphthalein was used in the titration.

The potassium salt of phenylsulfonamidophosphoryl chloride $C_6H_5SO_2NKPOCl_2$ formed elongated plates from ethyl alcohol; yield 94 %, decomp. point 197-198°.

Found %: Cl 22.49, 22.55; K 12.50. Equiv. after hydrolysis 2.98, 2.97. $C_6H_5O_3NSPCl_2K$.
Calculated %: Cl 22.75; K 12.60. Equiv. after hydrolysis 3.00.

The potassium salt of p-tolylsulfonamidophosphoryl chloride, $p\text{-}CH_3C_6H_4SO_2NKPOCl_2$ formed prisms from methyl alcohol; yield 51.0 %, decomp. point 210-213°.

Found %: Cl 21.58, 21.68; N 4.30, 4.51. Equiv. after hydrolysis 2.93, 2.95. $C_7H_7O_3NSPCl_2K$.
Calculated %: Cl 21.77; N 4.29. Equiv. after hydrolysis 3.00.

The potassium salt of p-chlorophenylsulfonamidophosphoryl chloride, $p\text{-}ClC_6H_4SO_2NKPOCl_2$, formed plates from ethyl alcohol and needles from water; yield 83 %, decomp. point 207-208°.

Found %: Cl 30.46, 30.70; K 11.64, 11.82. $C_6H_4O_2NSPCl_3K$. Calculated %: Cl 30.73; K 11.25.

The potassium salt of o-nitrophenylsulfonamidophosphoryl chloride, $o\text{-}NO_2C_6H_4SO_2NKPOCl_2$ formed needles from ethyl alcohol; yield ~ 100%, decomp. point 199-200°.

Found %: Cl 19.99, 19.67; N 7.98, 8.05. Equiv. after hydrolysis 3.12, 3.15. $C_6H_4O_5N_2SPCl_2K$.
Calculated %: Cl 19.88; N 7.84. Equiv. after hydrolysis 3.00.

The potassium salt of p-nitrophenylsulfonamidophosphoryl chloride, $p\text{-}NO_2C_6H_4SO_2NKPOCl_2$, formed prisms from ethanol; yield 87.0%, decomp. point 190-192°.

Found %: Cl 19.77, 19.97; N 8.02, 8.09. Equiv. after hydrolysis 2.98, 2.92. $C_6H_4O_5N_2SPCl_2K$.
Calculated %: Cl 19.88; N 8.67. Equiv. after hydrolysis 3.00.

The potassium salt of m-nitrophenylsulfonamidophosphoryl chloride, $m\text{-}NO_2C_6H_4SO_2NKPOCl_2$, formed prisms from ethyl or methyl alcohol; yield ~ 100 %. m.p. 205-206°.

Found %: Cl 19.65, 19.58; N 7.93, 8.02. Equiv. after hydrolysis 2.96. $C_6H_4O_5N_2SPCl_2K$.
Calculated %: Cl 19.88; N 7.84. Equiv. after hydrolysis 3.00.

The aniline salt of phenylsulfonamidophosphoryl chloride. On mixing ether solutions of equivalent amounts of phenylsulfonamidophosphoryl chloride and aniline, the product precipitated immediately as large, needlelike crystals. The yield was 97.0%. After recrystallization from chloroform, the long needles had m.p. 107-110°.

Found %: N 7.57, 7.75. $C_{12}H_{13}O_3N_2SPCl_2$. Calculated %: N 7.62.

Hydrolysis of trichlorophosphazosulfonephenyl with potassium carbonate solution. 0.01 mole of trichlorophosphazosulfonephenyl was added to a solution of 5 g of potassium carbonate in 10 ml of water. Evolution of

heat occurred and the character of the precipitate changed. After cooling, the reaction product was filtered off, pressed out between sheets of filter paper and recrystallized from ethyl alcohol. The yield was 1.7 g (54.0%), decomp. point 197-198°. The compound did not depress the melting point of the potassium salt of phenylsulfonamidophosphoryl dichloride, prepared from phenylsulfonamidophosphoryl dichloride.

Reactions of the potassium salts of arylsulfonamidophosphoryl chlorides with sodium methylate. A solution of sodium methylate (0.02 mole) in methyl alcohol was slowly added to a suspension of 0.01 mole of the potassium salt of the arylsulfonamidophosphoryl chloride in methyl alcohol. After some time the alcohol was distilled off in a water pump vacuum. The residue was dissolved in water. The reaction product was isolated by acidifying the aqueous solution with hydrochloric acid.

Dimethyl phenylsulfonamidophosphate. The yield was 93.0% and the m.p. 106-108°, which corresponds to literature data [4].

Dimethyl p-chlorophenylsulfonamidophosphate. The yield was 60.0% and the m.p. 128-129°. The compound did not depress the melting point of the product, obtained from the reaction of sodium methylate and p-chlorophenylsulfonamidophosphoryl chloride.

Dimethyl m-nitrophenylsulfonamidophosphate. The yield was 83.0% and the m.p. 150-151°. The compound did not depress the melting point of the dimethyl m-nitrophenylsulfonamidophosphate, obtained by treating m--nitrophenylsulfonamidophosphoryl dichloride with sodium methylate.

Trichlorophosphazosulfone-p-chlorophenyl, $p\text{-}ClC_6H_4SO_2N{=}PCl_3$. A mixture of 0.01 mole of p-chlorophenylsulfonamide and 0.01 mole of phosphorus pentachloride was heated on an oil bath at 100-105° until hydrogen chloride was no longer evolved (1.5 hours). After cooling the clear, mobile liquid crystallized. The yield was 32.6 g (~ 100%). The compound crystallized from petroleum ether as large, lustrous plates with m.p. 71-73°. The product was readily soluble in benzene, ether and hot petroleum ether.

Found: equiv. after hydrolysis 4.93, 4.96. $C_6H_4O_2NSCl_4P$. Calculated: equiv. after hydrolysis 5.00.

p-Chlorophenylsulfonamidophosphoryl dichloride $p\text{-}ClC_6H_4SO_2NHPOCl_2$. 0.15 mole of glacial acetic acid was added to a solution of 0.1 mole of trichlorophosphazosulfone-p-chlorophenyl in 20 ml of benzene. The hydrolysis product, which precipitated after some time, was sucked off after 6 hours; they yield was 2.7 g (90.0%). The compound crystallized from benzene as fine needles with m.p. 148-150°.

Found: equiv. after hydrolysis 3.93, 3.98. $C_6H_5O_3NSPCl_3$. Calculated: equiv. after hydrolysis 4.00.

Trimethoxyphosphazosulfone-p-chlorophenyl and dimethyl p-chlorophenylsulfonamidophosphate. A solution of sodium methylate in methyl alcohol (from 0.075 mole of sodium and 30 ml of methanol) was added slowly with cooling to a solution of 0.025 mole of trichlorophosphazosulfone-p-chlorophenyl in benzene. The sodium chloride precipitate was filtered off after some time, the benzene and methyl alcohol distilled off, the residue treated with water and the oil thus liberated, extracted with ether. The ether solution was dried with sodium sulfate and then ether distilled off. After removal of the ether, the residual product crystallized on cooling; the yield was 3.2 g (41.0%). The substance formed plates from petroleum ether with m.p. 51-52°.

Found %: Cl 11.55, 11.69; N 4.71, 4.84. $C_9H_{13}O_5NSPCl$. Calculated %: Cl 11.32; N 4.46.

The aqueous extract (see previous experiment) was acidified with hydrochloric acid. The dimethyl p-chlorophenylsulfonamidophosphate precipitated as an oil, which quickly solidified; the yield was 1.4 g (20.0%). The compound crystallized from benzene as fine needles. If the crystals were left for a day in the solution, they changed into large, clear prisms with m.p. 129-130°.

Found %: Cl 12.17, 11.92. $C_8H_{11}O_5NSPCl$. Calculated %: Cl 11.85.

SUMMARY

It was shown that, inspite of the presence of active chlorine atoms in their molecules, arylsulfonamidophosphoryl dichlorides form stable potassium salts. The structure of the salts was proved by converting them into the dimethyl esters of arylsulfonamidophosphoric acids.

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THE REACTIONS OF FREE RADICALS IN SOLUTIONS

XII. INVESTIGATION OF THE MECHANISM OF THE INHIBITING ACTION OF POLYPHENOLS AND AROMATIC AMINES ON THE PROCESS OF THE INITIATION OF POLYMERIZATION

B. A. Dolgoplosk and G. A. Parfenova

Polyphenols and aromatic amines are widely used as inhibitors of the processes of initiated polymerization and oxidation.

In spite of a considerable number of investigations in this field the mechanism of the inhibiting action of these compounds has remained insufficiently clear up to the present. The majority of investigators assume that the inhibiting action of phenols and aromatic amines is caused by their direct reaction with peroxides, hydroperoxides or initial active centers, which are the source of the development of a chain process. In previous works carried out it was established that in the case of the thermal polymerization of styrene, polyphenols and aromatic amines do not act as inhibitors of the process themselves; their inhibiting action is only shown in the presence of oxygen or salts of metals of variable valence which oxidize polyphenols and aromatic amines into the corresponding quinones [1-3].

The present investigation showed that these conclusions may also be fully applied to the case of the initiated polymerization of various monomers.

Various compounds, able to decompose on heating to form free radicals, were used as initiators of the polymerization process: the dinitrile of azoisobutyric acid, diazoaminobenzene, methylphenyltriazene, isopropylbenzene hydroperoxide and benzoyl peroxide.

As the inhibiting action of aromatic amines and polyphenols could be directly associated with the nature of their reaction with polymeric radicals it was necessary to investigate monomers which form radicals of different activity.

Of the monomers giving highly active radicals, vinyl acetate and allyl acetate were used; chloroprene, isoprene and styrene were used to obtain polymeric radicals of low activity. Methylmethacrylate was intermediate in position, as regards activity, between these two groups. Hydroquinone, diphenylamine and phenyl-β-naphthylamine (neozone D) were tested as inhibitors of polymerization, the concentration employed being 0.5 mole per mole of initiator.

Fig. 1 gives the experimental data on the kinetics of the polymerization of styrene in the presence of hydroquinone and diphenylamine in a medium of nitrogen during the initiation of the process by various activators.

From the results given it follows that in the absence of oxygen, hydroquinone and diphenylamine in every instance exert no influence at all on the kinetics of the polymerization of styrene. Similar results were obtained in the polymerization of other monomers (chloroprene, isoprene, methylmethacrylate) under the influence of the dinitrile of azoisobutyric acid in the presence of hydroquinone and phenyl-β-naphthylamine (Fig. 2).

Not one of the compounds tested caused the appearance of induction periods or influenced the rate of polymerization. In the case of styrene, isoprene and chloroprene, the inhibitor content was 0.5 mole per mole of initiator while in the case of methylmethacrylate it was increased to 2 moles per mole of activator.

The decomposition reaction of the dinitrile of azoisobutyric acid (0.0033 mole) in the presence of hydroquinone (0.0065 mole) in a solution of dioxan was studied for 5 hours. It was shown that under these conditions

the amount of hydroquinone remains unaltered although the dinitrile is completely decomposed. This fact shows that the dimethylcyanomethyl radicals formed by the decomposition of the dinitrile cannot react with hydroquinone. The influence of hydroquinone during the polymerization of vinyl acetate and allyl acetate was found to be rather different. In this case although hydroquinone did not produce an induction period it did appreciably reduce the rate of the process (Fig. 3).

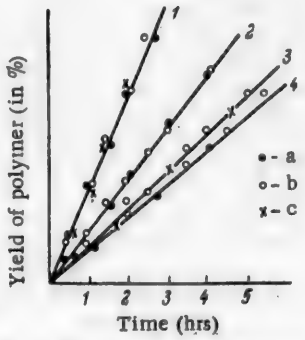


Fig. 1. Polymerization of styrene under the influence of various initiators in the presence of hydroquinone and diphenylamine in a medium of nitrogen.
1) The dinitrile of azoisobutyric acid at 70°, 2) benzoyl peroxide at 70°, 3) diazoaminobenzene at 100°, 4) isopropylbenzene hydroperoxide at 80°.
a) Without initiator, b) with hydroquinone, c) with diphenylamine.

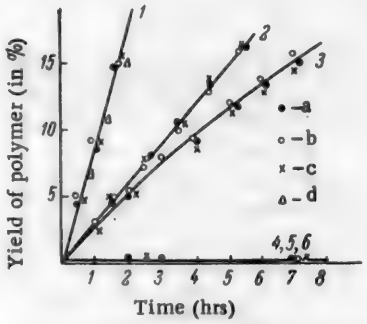
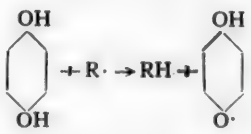


Fig. 2. Polymerization of various monomers under the influence of the dinitrile of azoisobutyric acid in the presence of hydroquinone, diphenylamine and phenyl-β-naphthylamine in nitrogen and air.
1) Chloroprene, 2) methylmethacrylate, 3) isoprene.
a) Without inhibitor, b) with hydroquinone, c) with diphenylamine, d) with phenyl-β-naphthylamine.
1,2,3) in nitrogen, 4,5,6) in air.

Vinyl acetate and allyl acetate form very active polymeric radicals which can react at a definite rate with hydroquinone with the formation of stable semiquinoid radicals, inhibiting polymerization.



The polymeric allyl radicals formed during the polymerization of isoprene and chloroprene and also the benzyl radicals formed during the polymerization of styrene do not react with hydroquinone because of their relatively low activity.

The character of the action of polyphenols and aromatic amines in the polymerization process is markedly different in the presence of oxygen. For example, during the polymerization of styrene under the influence of peroxides, hydroperoxides, azo- and diazoamino compounds, the presence of 0.5 mole of hydroquinone per mole of initiator causes the appearance of induction periods of varying duration (Fig. 4).

This phenomenon cannot be explained by the inhibiting action of oxygen itself because in the presence of hydroquinone oxygen does not retard but rather accelerates the polymerization process. This fact indicates that conceptions to the effect that oxygen inhibits polymerization because of the formation of low-active radicals, according to the reaction $R\cdot + O_2 \longrightarrow ROO$, are not sufficiently well founded. The appearance of induction periods and yellow solutions in the presence of oxygen must be explained by the influence of quinoid compounds formed under the influence of the primary reaction products of oxygen and olefins. Complete inhibition of the process in the presence of hydroquinone, phenyl-β-naphthylamine and diphenylamine is also found during the polymerization of other monomers in the presence of air: methylmethacrylate (Fig. 2, Curves 4-6) and vinyl acetate (Fig. 3, Curve 3).

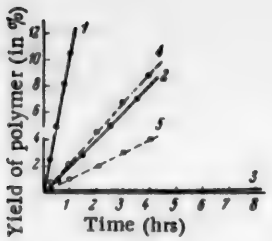
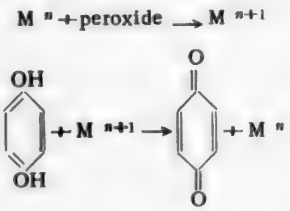


Fig. 3. Polymerization of allyl acetate and vinyl acetate under the influence of the dinitrile of azoisobutyric acid in the presence of hydroquinone in a medium of nitrogen and air. 1) Vinyl acetate without hydrogen in nitrogen at 50°, 2) vinyl acetate with hydroquinone in nitrogen at 50°, 3) vinyl acetate with hydroquinone in air at 50°, 4) allyl acetate without hydroquinone in nitrogen at 80°, 5) allyl acetate with hydroquinone in nitrogen at 80°.

The conclusion that the inhibition of the process is not directly connected with the action of oxygen is also substantiated by the fact that the replacement of oxygen by another oxidizer capable of oxidizing hydroquinone in a medium of nitrogen causes the inhibition of polymerization. This action is also observed during the initiation of the process by benzoyl peroxide, isopropylbenzene hydroperoxide or diazoaminobenzene in a nitrogen medium in the presence of hydroquinone and very small amounts of manganese naphthenate (Fig. 5).

In this instance the inhibition of the process is caused by the oxidation of hydroquinone into quinone by the salts of metals of variable valence (according to the system shown below).

Because of the reversibility of the system very low concentration of metallic salts are effective. In contrast to peroxides, hydroperoxides and diazoamino compounds, azo compounds and, in particular, the dinitrile of azoisobutyric acid do not take part in oxidative-reductive conversions and are not decomposed under the influence of salts of metals of variable valence, as a result of which the polymerization process takes place without an induction period.



It is evident, therefore, that the true inhibitors of the process of initiated polymerization are not polyphenols but aromatic amines and their oxidation products.

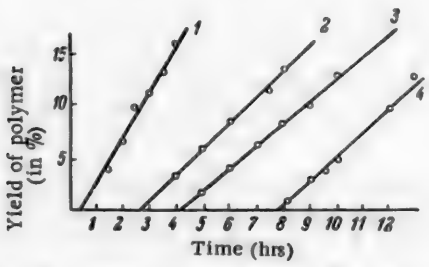


Fig. 4. Polymerization of styrene in the presence of hydroquinone in a medium of air.
1) Dinitrile of azoisobutyric acid at 70°,
2) isopropylbenzene hydroperoxide at 80°,
3) benzoyl peroxide at 70°,
4) diazoaminobenzene at 100°.
Content of inhibitor 0.0050 mole, of initiator 0.0025 mole.

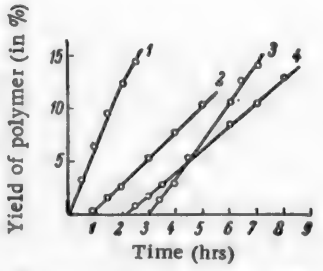


Fig. 5. Polymerization of styrene with various initiators in the presence of hydroquinone and manganese naphthenate in a nitrogen medium.
1) Dinitrile of azoisobutyric acid at 70°,
2) diazoaminobenzene at 100°, 3) benzoyl peroxide at 70°, 4) isopropylbenzene hydroperoxide at 100°.
Content: initiator 0.005 mole, hydroquinone 0.002 mole, Mn naphthenate 0.043 g/liter.

The conclusion that the mechanism of the inhibiting action of polyphenols and aromatic amines is associated with their conversion to quinoid structures receives strong confirmation in the inhibiting action of the quinones themselves.

EXPERIMENTAL

Styrene was washed with a 5 % solution of alkali, then dried and distilled in a current of nitrogen and the fraction with a boiling point of 31-32° at 9 mm was selected; the styrene content in this fraction, determined by the iodometric method [4], was 99.8-100.0%.

Methylmethacrylate was washed with a 5 % solution of alkali and dried with calcined sodium sulfate. The fraction selected during distillation was that with a b.p. of 61-62° at 200 mm. This fraction was further dried with anhydrous copper sulfate. The methylmethacrylate content determined by saponification with caustic alkali was 99.7-101.1 %.

Vinyl acetate. The method generally employed for purifying vinyl acetate – by distillation of the latter from a partially polymerized mixture – did not ensure the required purity of the product in this instance. The vinyl acetate was first washed with alkali, dried with calcined sodium sulfate and then distilled with an efficient laboratory distillation column, the sample boiling at 72.6° and 760.5 mm (n_D^{20} 1.3950) being selected. The vinyl acetate content determined by saponification with alkali was 99.0-99.6 %.

Allyl acetate was treated with alkali, dried and distilled; the fraction with a b.p. of 53-54° at 124-125 mm was selected.

Chloroprene was first freed from stabilizer by distillation in nitrogen at reduced pressure; it was then washed with alkali, dried and again distilled.

Isoprene was distilled with an efficient distillation column, the fraction boiling at 34.4° being selected. The isoprene content was over 99 %.

Methylphenyltriazene was synthesized by Dimroth's method [5].

The dinitrile of azoisobutyric acid was obtained by Dox's method [6].

The filling of the ampoule and the polymerization process were carried out under conditions which virtually excluded the entry of oxygen [7]. The kinetics of the polymerization process were studied by the dilatometer method and the final yield of polymer was determined gravimetrically.

SUMMARY

1. The influence of hydroquinone, phenyl-β-naphthylamine and diphenylamine on the polymerization of various mono- and diolefins, initiated by various activators, was investigated.

It was established that in the absence of oxygen the above-mentioned compounds exert no influence on the kinetics of polymerization.

Some reduction in the polymerization rate was only observed in the case of monomers which form highly-active polymeric radicals (vinyl acetate, allyl acetate).

2. The inhibiting action of polyphenols and aromatic amines is only fully shown in the presence of oxygen or other compounds, ensuring their oxidation to quinoid forms.

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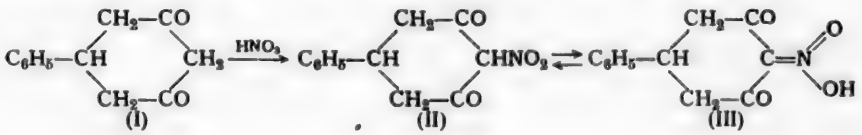
2-NITRO-5-PHENYL-1,3-CYCLOHEXANEDIONE AND ITS DERIVATIVES

E. Yu. Gudriniece, D. K. Kurgan and G. Ya. Vanags

Continuing our investigations in the field of nitro derivatives of cyclic β-diketones we undertook the study of 5-phenyl-1,3-cyclohexanedione, the structure of which resembles dimedone (5,5-dimethyl-1,3-cyclohexanedione). 5-Phenyl-1,3-cyclohexanedione has been far less studied than dimedone. The best known of the derivatives of 5-phenyl-1,3-cyclohexanedione are those obtained by the substitution of the hydrogen atoms of the active methylene group [1-6]. Nitro derivatives of 5-phenyl-1,3-cyclohexanedione are unknown.

5-Phenyl-1,3-cyclohexanedione is a readily obtainable compound. Its synthesis [7, 8] is simpler than that of dimedone. 5-Phenyl-1,3-cyclohexanedione is obtained by condensing benzalacetone with malonic ester. In the course of the work we improved the method given in literature for its preparation, reducing the time for the condensation from 7 hours to 15-30 minutes. The product obtained was fairly pure and we used it for subsequent work without recrystallization. The m.p. was 184-185° (literature data 183-184°).

The same method as that which we used for dimedone [9] was found to be suitable for the nitration of 5-phenyl-1,3-cyclohexanedione(I). The 2-nitro-5-phenyl-1,3-cyclohexanedione (II) obtained was a yellow crystalline substance. At 20° approximately 5 g dissolved in a liter of water, forming a greenish-yellow solution. The aqueous solution was a strong acid, liberating carbon dioxide from carbonates and hydrogen sulfide from sulfides; a concentrated solution also liberated acetic acid from acetates. It is possible that in an aqueous solution (II) exists in the aci- form, or, more precisely, in the form of a nitronic acid (III).



When recrystallized from water or benzene, (II) melted at 119-120° (decomp.); if precipitated from a saturated aqueous solution by hydrochloric acid it melted at 129° (decomp.).

Being a strong acid, (II) easily formed salts. The sodium, potassium and ammonium salts which were made were yellow crystalline substances readily soluble in water. When heated they decomposed violently. Just as the nitroindandione [10], nitroperinaphthindandione [11] and nitrodimedone [9] salts of bivalent iron are different in color and properties from all the other salts so the nitrophenylcyclohexanedione salt of bivalent iron gave a dark-red alcoholic solution; when diluted with water the solution became yellow. It was not possible to isolate this salt in the solid form.

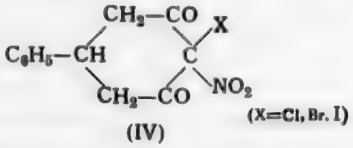
Several salts of nitrophenylcyclohexanedione with organic bases were also prepared. These were yellow or colorless crystalline substances, soluble to a greater or lesser extent in water. The salts of nitrophenylcyclohexanedione are, therefore, less suitable for identifying amines than the salts of nitroindandione [10].

In contrast to nitroparaffins [12] 2-nitro-5-phenyl-1,3-cyclohexanedione does not condense with aldehydes in exactly the same way as nitrodimedone [9].

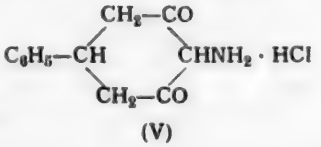
Like many other compounds with an active methylene group [9, 11, 13-16], (II) is readily halogenated, forming 2-halogen-2-nitro-5-phenyl-1,3-cyclohexanedione (IV). We carried out the halogenation with both free and combined halogen. It was found that excess chlorine and bromine was undesirable for the halogenation reaction

because the corresponding halogen derivatives split up both in aqueous solution or in glacial acetic acid, forming β-phenylglutaric acid and halonitromethanes (up to chloro- or bromopicrin). Iodonitrophenylcyclohexanedione was prepared by the iodination of (II) with dioxan-bisiodochloride [19] in glacial acetic acid.

In both 2-halogen-2-nitro-5-phenylcyclohexanediones and 2-halogen-2-nitrodimedones [19] the halogen is combined in an unstable manner. It acts on aromatic amines in a halogenizing manner. Water and, in particular, alkali readily splits off the halogen as halogen acid. The more electropositive the halogen the less the energy of activation required to rupture the C-halogen bond and the less stable the halogen derivative. The least stable is 2-iodo-2-nitro-5-phenyl-1,3-cyclohexanedione, which splits off iodine on keeping for 1-2 days.



(IV)



(V)

With excess hydroxylamine hydrochloride, (II) gives a monoxide. It was not possible to obtain the dioxide although nitroindandione dioxide has recently been prepared [17]. With semicarbazide it gives a monosemicarbazone. It was difficultly soluble in water.

2-Amino-5-phenyl-1,3-cyclohexanedione hydrochloride (V) was prepared by reducing 2-nitro-5-phenylcyclohexanedione with tin and hydrochloric acid by the method described for preparing nitrodimedone. In glacial acetic acid and in the presence of sodium acetate it gives a dark blue color with bindone [18]. The investigation of this substance is continuing.

EXPERIMENTAL

5-Phenyl-1,3-cyclohexanedione (I). a) The sodium salt of the ethyl ester of 5-phenyl-1,3-cyclohexanedione-4-carboxylic acid. 80 ml of malonic ester was added to a solution of sodium ethylate in a round-bottomed flask, prepared by dissolving 11.5 g of sodium in 100 ml of anhydrous alcohol; 71 g of benzalacetone was then added with cooling. A vigorous reaction commenced after only 5 minutes heating on a water bath. Heating was continued for a further 15-30 minutes. The light-yellow salt formed was washed with ether. The yield was 130.5 g (92.1 %).

b) 5-Phenyl-1,3-cyclohexanedione (I). 130.5 g of the sodium salt obtained was dissolved in 0.5 liters of water and boiled for 25-30 minutes with 20 g of caustic soda. Activated carbon was added and mixture was cooled. When the filtrate was acidified, 5-phenyl-1,3-cyclohexanedione-4-carboxylic acid was precipitated. The latter was suspended in 0.4-0.5 liters of water and was boiled in a large flask. A vigorous evolution of carbon dioxide took place and 5-phenyl-1,3-cyclohexanedione was precipitated. After the evolution of carbon dioxide had ceased the precipitate was filtered. The yield was 72 g (75.5 %), the m.p. was 184-185°. It was insoluble in water and could be recrystallized from glacial acetic acid.

2-Nitro-5-phenyl-1,3-cyclohexanedione (II). 7.5 ml of fuming nitric acid (d 1.54) was added dropwise to 15 g of (I) in 60 ml of absolute ether in a three-necked round-bottomed flask, equipped with a mechanical stirrer, reflux condenser and dropping funnel, the mixture being cooled with ice and salt and stirred vigorously. Stirring was continued for a further 10-15 minutes. The product obtained was washed several times on a filter with ether. The yield was 17.3 g (93 %) of finely-crystalline (II). The m.p. was 117-119° (decomp.). It was readily soluble in alcohol, acetone, chloroform, dioxan and glacial acetic acid and insoluble in ether, carbon tetrachloride and gasoline. It crystallized well from water in the form of fine yellow crystals. The m.p. was 119-120° (decomp.).

Found %: N 5.82, 5.93. $C_{12}H_{11}O_4N$. Calculated %: N 6.01.

Salts of 2-nitro-5-phenyl-1,3-cyclohexanedione (II).

Sodium salt. This was obtained by boiling (II) with sodium carbonate in an alcoholic solution. After the addition of ether the yellow sodium salt was precipitated from the filtrate and this was crystallized from a small amount of alcohol. It melts at 255-260°, becoming ignited.

Found %: N 5.37, Na 8.96. $C_{12}H_{10}O_4NNa$. Calculated %: N 5.49; Na 9.20.

Potassium salt. This was obtained in a similar manner to the sodium salt. It was in the form of greenish-yellow fine crystals. When heated it decomposed violently.

Found %: N 5.28. $C_{12}H_{10}O_4NK$. Calculated %: N 5.17.

Ammonium salt. This was prepared by passing ammonia into an alcoholic solution of (II). It was crystallized from a mixture of alcohol and benzene. It was in the form of yellow crystals. The m.p. was 204-205° (decomp.).

Found %: N 11.07. $C_{12}H_{14}O_4N_2$. Calculated %: N 11.20.

Salts of (II) with organic bases were prepared in a solution of alcohol or benzene by the addition of the corresponding amine or by dissolving (II) in an excess of amine (see Table 1).

TABLE 1

Salts of 2-Nitro-5-phenyl-1,3-cyclohexanedione with Organic Bases.

Expt. No.	Base	Solvent	Recrystallized from	Melting point of the salt	Color	Empirical molecular formula	Nitrogen content (as %)	
							Found	Calculated
1	Aniline	Alcohol	Alcohol	134°	Yellow	$C_{18}H_{18}O_4N_2$	8.84	8.59
2	o-Toluidine	Alcohol	Alcohol + ether	139-141	White	$C_{19}H_{20}O_4N_2$	8.22	8.24
3	m-Toluidine	Benzene	Anhydrous alcohol	153-154	White	$C_{19}H_{20}O_4N_2$	8.33	8.24
4	p-Toluidine	Benzene	Anhydrous alcohol	152	Yellow	$C_{19}H_{20}O_4N_2$	8.23	8.24
5	β-Naphthyl-amine	Alcohol	Water	167-169	White	$C_{22}H_{20}O_4N_2$	7.80	7.45
6	Piperidine	Piperidine	Benzene	128-130	Greenish	$C_{17}H_{22}O_4N_2$	8.59	8.80
7	Pyridine	Pyridine	Anhydrous alcohol	156-157	Yellow	$C_{17}H_{18}O_4N_2$	8.86	8.97

2-Chloro-2-nitro-5-phenyl-1,3-cyclohexanedione (IV, X = Cl). A cooled solution of 0.5 g of (II) in 7 ml of glacial acetic acid was saturated with chlorine and diluted with water until an opalescence appeared. White needles of 2-chloro-2-nitro-5-phenyl-1,3-cyclohexanedione were precipitated on standing. The yield was 0.49 g (84%), the m.p. was 125-126°. It was readily soluble in ether, alcohol, acetone and glacial acetic acid but only slightly soluble in carbon tetrachloride and gasoline; it was insoluble in water but split off an atom of chlorine in the form of hypochloric acid. It was stable in air.

Found %: N 4.96. $C_{12}H_{10}O_4NCl$. Calculated %: N 5.23.

2-Bromo-2-nitro-5-phenyl-1,3-cyclohexanedione (IV, X = Br). 1.1 g of dioxan dibromide, dissolved in 5 ml of glacial acetic acid, was added with cooling to 1 g of (II) in 10 ml of glacial acetic acid. 1.3 g (98.5%) of 2-bromo-2-nitro-5-phenyl-1,3-cyclohexanedione was precipitated as fine colorless crystals by the addition of water. The m.p. was 119-120°; it was readily soluble in ether, alcohol, dioxan , chloroform, glacial acetic acid and benzene. It was possible to recrystallize it from a mixture of gasoline and carbon tetrachloride. When acted on by water it was rapidly hydrolyzed.

Found %: N 4.18. $C_{12}H_{10}O_4NBr$. Calculated %: N 4.48.

2-Iodo-2-nitro-5-phenyl-1,3-cyclohexanedione (IV, X = I). 0.44 g of a complex consisting of dioxan and 2 molecules of iodine chloride [19] was added to a solution of 0.5 g of (II) in 10 ml of glacial acetic acid and after 3-5 minutes the mixture was diluted with a small amount of water. 2-Iodo-2-nitro-5-phenyl-1,3-cyclohexanedione was precipitated as yellow platelets. The yield was 0.68 g (77.2 %). It turned red at 125° and melted at 141-142°(decomp.) with the evolution of violet iodine vapor. It was readily hydrolyzed in water.

Found %: N 3.61. $C_{12}H_{10}O_4NI$. Calculated %: N 3.90.

Monosemicarbazone of 2-nitro-5-phenyl-1,3-cyclohexanedione. 1 g of (II) in 20 ml of anhydrous alcohol was heated for 30 minutes on a water bath with a solution of semicarbazide, prepared from 0.48 g of semicarbazide hydrochloride and 0.36 g of anhydrous sodium acetate. The yield was 0.94 g (75.8%) of the yellow finely-crystalline monosemicarbazone of (II). It was insoluble in ether and acetone but soluble in acetic acid. After

recrystallization from alcohol it was in the form of yellow platelets with an m.p. of 194° (decomp.).

Found %: N 19.45, 19.52. $C_{13}H_{14}O_4N_4$. Calculated %: N 19.37.

Monoxime of 2-nitro-5-phenyl-1,3-cyclohexanedione. 0.75 g of hydroxylamine hydrochloride in 1-2 ml of water was added to 0.5 g of nitrophenylcyclohexanedione in 30 ml of water. A light-yellow precipitate of monoxime was formed after 24 hours. When heating was employed the reaction took place rapidly. The yield was quantitative. It was insoluble in ether, dioxan , chloroform and ethyl acetate, difficultly soluble in alcohol and readily soluble in glacial acetic acid but with partial decomposition. It crystallized from methanol as light-yellow platelets. The m.p. was 191° (decomp.).

Found %: N 11.41. $C_{12}H_{12}O_4N_2$. Calculated %: N 11.20.

2-Amino-5-phenyl-1,3-cyclohexanedione (V). 5 g of (II), 20 ml of concentrated hydrochloric acid and 7 g of tin cuttings were heated until a solution was obtained. The solution had a red color. When it was cooled tin was precipitated as the sulfide and the solution was evaporated until crystals appeared. The yield was 2.4 g (46.1%) of 2-amino-5-phenyl-1,3-cyclohexanedione hydrochloride. Long colorless needles were obtained from alcohol with the addition of ether. The m.p. was 210-213° (decomp.).

Found %: N 5.96. $C_{12}H_{14}O_2NCl$. Calculated %: N 5.85.

SUMMARY

1. The method of preparing 5-phenyl-1,3-cyclohexanedione was improved and a method for obtaining its 2-nitro-5-phenyl-1,3-cyclohexanedione derivative, not previously described in literature, was developed.

2. A number of derivatives of 2-nitro-5-phenyl-1,3-cyclohexanedione were prepared: salts with inorganic and organic bases, 2-halogen-2-nitro-5-phenyl-1,3-cyclohexanediones (halogens — chlorine, bromine, iodine), monosemicarbazone, monoxime and 2-amino-5-phenyl-1,3-cyclohexanedione hydrochloride.

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THE PREPARATION AND PROPERTIES OF SOME DERIVATIVES OF THIOXANTHENE-5-DIOXIDE WITH INDICATOR PROPERTIES

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Derivatives of thioxanthene-5-dioxide have been comparatively little studied. They are usually obtained by the oxidation of the corresponding derivatives of thioxanthone followed by the reduction of the carbonyl group [1-4]. In some instances they are secondary products in the process of the sulfonation of certain aromatic compounds [5, 6].

It was of interest to investigate the possiblity of obtaining various derivatives of thioxanthene-5-dioxide with a high yield by sulfonating certain aromatic derivatives.

The investigation was commenced by sulfonating diphenylmethane with 66% oleum. After the neutralization of the excess acid it was found that in alkali the solution had an intense yellow-orange color. The color disappeared when the solution was acidified. The subsequent investigation was directed at studying the nature of the colored compounds with indicator properties obtained by sulfonation.

Data are given in literature on the sulfonation of diphenylmethane, 1,1-diphenylethane, triphenylmethane and their derivatives [7-10]. By the action of various sulfonating agents on these hydrocarbons the authors obtained sulfonic acids which were converted into the corresponding hydroxy compounds by fusion with alkali. None of these works, however, give data on the formation of any substances with the above-described indicator properties.

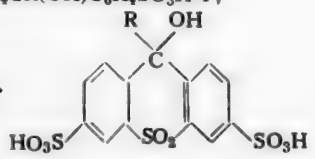
As we established, by the action of 66% oleum on diphenylmethane and its derivatives with intense cooling the methylene group is oxidized with simultaneous sulfonation in the 4,4' positions [7]. Under these conditions a small amount of red substance is already formed and this may be detected by the color of the alkalized solution of the sulfoproduct. It was not possible, however, to isolate it. By repeated recrystallization of the aniline salt of this sulfonic acid it is possible to obtain it completely free from the red substances. If the 4,4'-disulfonic acid of benzhydrol obtained is acted on by a fresh quantity of oleum at a temperature of 150-160° the red substance is obtained with a high yield.

Side by side with the sulfonation of diphenylmethane we carried out experiments on the sulfonation of 1,1-diphenylethane, triphenylmethane and 2,2-diphenylpropane under similar conditions. In all instances, except the latter, the formation of the red substances was observed. On the basis of these experiments the suggestion was made that for the formation of a substance with indicator properties the presence of at least one free hydrogen atom at the methylene group of hydrocarbons is required when oxidation occurs under sulfonation conditions.

By carrying out the sulfonation in the presence of a large excess of SO_3 the formation of a cyclic sulfone also may be expected [11]. The process of the reaction of 66% oleum with the above-mentioned hydrocarbons may, therefore, be represented according to the system:

$$(C_6H_5)_2CRH + SO_3(H_2SO_4) \longrightarrow 4\text{-}HO_3SC_6H_4CR(OH)C_6H_4SO_3H\text{-}4';$$

$$4\text{-}HO_3SC_6H_4CR(OH)C_6H_4SO_3H\text{-}4' + SO_3(H_2SO_4) \rightarrow$$



(I)

R=H, CH_3, C_6H_5

The structure of (I) was proven in the following manner: the thioxanthene-5-dioxide [4] obtained by the sulfonation of diphenylmethane with chlorosulfonic acid was treated with conc. H_2SO_4. At 40° the sulfone was sulfonated smoothly but no red color was formed. If a solution of the sulfone sulfonic acid in H_2SO_4 was heated until SO_3 was evolved the formation of the dye was observed when the solution was made alkaline. On the basis of this experiment we oxidized this sulfone by means of $Pb(CH_3COO)_4$ in glacial CH_3COOH. The result was the formation of a substance, insoluble in water but soluble in alcohol, which colored an alcoholic alkaline solution yellow.

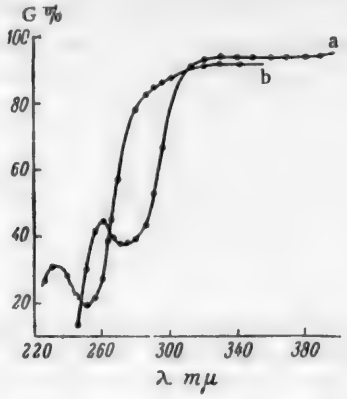


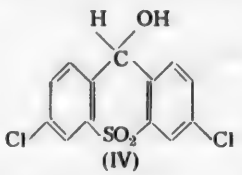
Fig. 1. Absorption curves in the ultraviolet region.
a) Aniline salt of thioxanthenol-5--dioxide-3,7-disulfonic acid (1 + + $2C_6H_5NH_2$) – aqueous NaOH, pH 11.7; b) thioxanthenol-5-dioxide-alcoholic NaOH, pH 11.7.

As may be seen from Fig. 1, the absorption curve of light in the ultraviolet region of this compound is similar in form to the curve of the substance obtained by the sulfonation of diphenylmethane.*

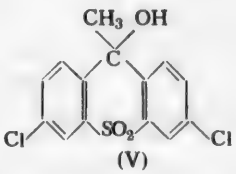
The oxidation of thioxanthene-5-dioxide with CrO_3 in CH_3COOH leads to the formation of thioxanthone-5--dioxide which does not have indicator properties.

We further proved the structure of the coloring matter by sulfonating a mixture of ortho- and para-dichlorosubstituted diphenylmethane and diphenylethane.

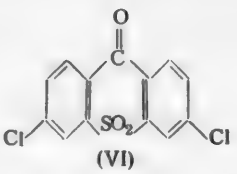
The mixture of dichlorophenylmethanes was obtained by reacting chlorobenzene with α,α'-dichloromethyl ester in the presence of $AlCl_3$, by analogy with the method previously described [14]. It was not possible to separate the mixture of isomers by distillation. If a mixture of this type is acted on by 20% oleum in the cold and the sulfonation product is poured into water, a water-insoluble product is obtained which crystallizes from hot alcohol and has indicator properties: it has a yellow color in alcoholic alkali and on acidification with CH_3COOH the color disappears. From its sulfur, chlorine and hydroxyl group contents the substance obtained (m.p. 166-167°) corresponds to the formula $C_{13}H_8O_2Cl_2S$. Structure (IV) may be attributed to it. This compound can be obtained from 4,4'-dichlorodiphenylmethane since the 4,4' positions are occupied by chlorine atoms. Under these conditions sulfonation of the sulfone formed does not take place. With further action on (IV) by oleum of higher concentration and at a higher temperature sulfonation occurs and the substance becomes soluble in water. If oleum is allowed to act under similar conditions on a mixture of the isomers of dichlorodiphenylethane, synthesized according to Tsukervanik [15], a compound is obtained with an m.p. of 146-147° and having the indicator properties of structure (V).



(IV)



(V)



(VI)

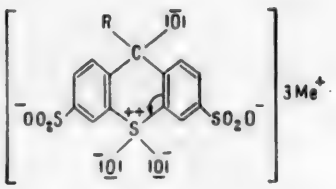
When (IV) and (V) are oxidized with CrO_3 in CH_3COOH the same substance (VI) is obtained. This has an m.p. of 251-252° and possesses the property, characteristic of the type of compound [17], of turning an alcoholic solution of NaOH into an intensely-blue color which disappears on shaking in air.

When diphenylmethane, 1,1-diphenylethane and triphenylmethane were sulfonated under similar conditions the corresponding derivatives of thioxanthenol-5-dioxide, having indicator properties, were obtained.

The isolated compounds, obtained by the sulfonation of these aromatic hydrocarbons have a number of remarkable properties: a) in a strongly-alkaline medium in the presence of air or negligible amounts of H_2O_2 the

*The investigations connected with the preparation and properties of thioxanthenol-5-dioxide [12,13] do not mention the indicator properties we discovered.

yellow color changes to intense green and then back again to yellow after a brief interval.* b) The hydroxyl group present is not benzoylated by benzoyl chloride or methylated by $(CH_3)_2SO_4$ in an alkaline medium. c) Only the hydrogen atoms of the sulfo group react with diazomethane, as a result of which methyl esters of the sulfonic acids are formed. d) The color change takes place at a pH of 11.5-12.5. Fig. 2 shows the absorption curves in the visible region of light in an alkaline medium.** In the ultraviolet region all the compounds have an absorption maximum at λ 270 mμ, both in an acid and an alkaline medium.



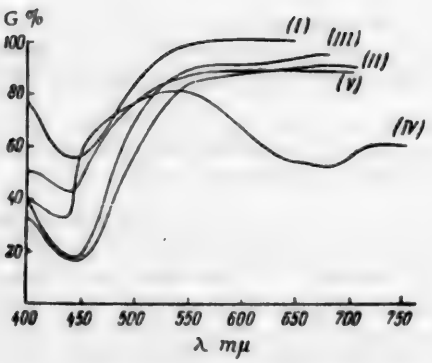
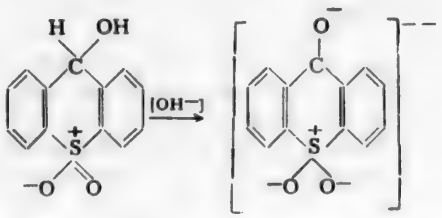


Fig. 2. Absorption curves in the visible region of the spectrum.
(I) – Thioxanthenol-5-dioxide-3,7-disulfonic acid, (II) – 10-Methylthioxanthenol-5-dioxide-3,7-disulfonic acid, (III) – 10(Sulfophenyl)--thioxanthenol-5-dioxide-3,7-disulfonic acid, (IV) – 3,7-Dichlorothioxanthenol-5-dioxide, (V) – 3,7-Dichloro-10-methylthioxanthenol--5-dioxide.
(I), (II) and (III) – in aqueous NaOH, pH 11.53; (IV) and (V) – in alcoholic KOH, pH 11.95.

The above-listed properties of the synthesized compounds can be explained on the assumption that a particular type of chromophoric group is formed.

The S atom combined with anaromatic ring has a positive charge because of the semipolar bond with oxygen [16]. On the other hand, the C–OH group is in the ortho position to the S atom. In an alkaline medium the latter may be converted into a $C-O^-$ anion. The negative charge of the oxygen passes over partially to the C atom. The benzene ring therefore has positively and negatively charged atoms in the ortho position and these can cause a quinoidlike polarization of the benzene ring. The proposed structure



of the colored form of thioxanthone-5-dioxide in alcoholic alkaline solution [12] does not explain the indicator properties of the compounds we investigated, in which the hydrogen of the methylene carbon is replaced by R.

The nature of the green color found with derivatives having an unsubstituted hydrogen atom can be explained by analogy with the blue color of thioxanthone-5-dioxide. This hypothesis requires further experimental confirmation.

EXPERIMENTAL

Sulfonation of diphenylmethane. 185 g of diphenylmethane with a b.p. of 130° at 12 mm was treated with 190 ml of 66% oleum. The addition of the oleum was made in such a way that the temperature did not exceed 120°. The mixture was then heated to 160-170° and a further 95 ml of oleum was added. The mixture was then kept at this temperature for 15-20 minutes. It was then cooled and poured into water. The excess H_2SO_4 was

* This phenomenon does not occur with derivatives in which one hydrogen atom at the CH_2 group is replaced by a radical.

** The spectra were determined by A. M. Fisher.

neutralized with $PbCO_3$. After the precipitate, consisting of $PbSO_4$ and excess $PbCO_3$, had been filtered the lead was precipitated by saturating the filtrate with H_2S. After the solution had been filtered it was evaporated on a water bath. 450 g of thioxanthenol-5-dioxide-3,7-disulfonic acid (I) was obtained, which crystallized out when allowed to stand in a desiccator over $CaCl_2$.

Freshly-distilled aniline was added to the solution of the sulfonic acid; this led to the formation of a copious crystalline precipitate of the aniline salt which was recrystallized from water. The crystals were in the form of needles and were difficultly soluble in cold water; they dissolved readily in alkali with the formation of an intense--yellow solution. The m.p. was 235° (in a copper melting point apparatus).

Found %: C 49.78, 50.90; H 4.17, 4.27; N 4.68, 4.73; S 16.05, 16.10. Neutralization equiv. of the aniline salt 295. $C_{25}H_{24}O_9N_2S_3$. Calculated %: C 50.60; H 4.05; N 4.74; S 16.20. Neutralization equiv. 295.

Benzhydrol 4,4'-disulfonic acid was obtained when 66% oleum was allowed to act on diphenylmethane with intense cooling and subsequent analogous treatment. The aniline salt crystallized as fine needles.

Found %: C 56.45, 56.61; H 5.28, 5.02; N 5.04, 5.10; S 12.54, 12.20. Neutralization equiv. of the aniline salt 267. $C_{25}H_{26}O_7N_2S_2$. Calculated %: C 56.60; H 4.92; N 5.29; S 12.05. Neutralization equiv. 265.

Sulfonation of 1,1-diphenylmethane. 10-methylthioxanthenol-5-dioxide-3,7-disulfonic acid (II) was obtained after the usual treatment from 65 g of 1,1-diphenylethane (b.p. 129° at 8 mm, n_D^{20} 1.5705, d_4^{20} 1.0057) and 110 ml of 66% oleum under conditions similar to those described above, at 160-165°.

Found %: C 51.66; H 4.61; N 4.78; S 15.20. Neutralization equiv. (benzidine salt) 306. $C_{20}H_{24}O_9N_2S_3$. Calculated %: C 51.70; H 3.98; N 4.65; S 15.90. Neutralization equiv. 302.

Sulfonation of triphenylmethane. 50 g of triphenylmethane was fused and treated with 50 ml of 66% oleum at 120°. It was then heated to 170° and a further 60 ml of oleum was added. After the usual treatment 125 g of a dry, dark, viscous mass was obtained. It was not possible to isolate salts with aniline, p-toluidine and benzidine. The potassium salt of 10-(sulfophenyl)-thioxanthenol-5-dioxide-3,7-disulfonic acid (III) was obtained by neutralizing the sulfonic acid with potash until it gave a weakly-acid reaction and then precipitating it with alcohol.

Found %: K 16.82. $C_{19}H_{11}O_{12}S_4K_3$. Calculated %: K 17.30.

Potassium salts of the aniline salts of (I) and (II) were obtained by neutralizing aqueous solutions of potash until a weakly-acid reaction was obtained, followed by steam distillation of the precipitated aniline and, after evaporation, precipitation of the salt with alcohol.

Preparation of dichlorodiphenylmethane. A mixture of 30 g of α,α'-dichlorodimethyl ester and 100 ml of chlorobenzene was added dropwise to a suspension of 60 g of $AlCl_3$ in 600 ml of chlorobenzene. The temperature rose to 45-50°. After the mixture had been run in, stirring was continued for 4-5 hours and it was left overnight. After the usual treatment the chlorobenzene was distilled off and the residue was distilled under vacuum. 98-100 g of a fraction boiling at 150-152° (2 mm) was obtained.

Found %: Cl 29.20. M 236 (cryoscopy). $C_{13}H_{10}Cl_2$. Calculated %: Cl 29.9. M 237.

Sulfonation of a mixture of isomers of dichlorodiphenylmethane. 100 g of the mixture obtained was treated with cooling with 25-30% oleum until the hydrocarbon layer disappeared and was poured into 2 liters of water containing ice. After some time 18-20 g of a dense white precipitate of 3,7-dichlorothioxanthenol-5-dioxide (IV) was formed.

After filtering and washing 15 g of (IV) was obtained with an m.p. of 166-167° (from alcohol) in the form of white shining platelets.

Found %: C 50.20; H 2.70; Cl 23.05; S 10.46; OH 5.54 (acetylation). M 316 (cryoscopy). $C_{13}H_8O_3Cl_2S$. Calculated %: C 49.60; H 2.54; Cl 23.20; S 10.10; OH 5.40. M 315.

Acetylation. 1.26 g of (IV) was treated with heating for 1 hour with a mixture of 10 ml of pyridine and 5 ml of acetic anhydride. The mixture was allowed to stand overnight and was then poured into acidified water. After dissolving in alcohol and precipitating with water 1.3 g of the acetyl derivative with an m.p. of 60-62° was obtained.

Found %: C 50.35; H 2.81; Cl 19.25; S 9.00. Saponification equiv. 180.0. $C_{15}H_{10}O_4Cl_2S$. Calculated%: C 50.50, H 2.08; Cl 19.90; S 9.00 Saponification equiv. 178.5.*

Sulfonation of dichloro-1,1-diphenylethane. 8 g of 3,7-dichloro-10-methylthioxanthenol-5-dioxide (V) with an m.p. of 146-147° (from alcohol) was obtained from 50 g of dichloro-1,1-diphenylethane and 25-30% oleum with cooling and further similar treatment.

Found %: C 51.52; H 3.00; Cl 21.00; S 10.20. M 325 (cryoscopy). $C_{14}H_{10}O_3Cl_2S$. Calculated %: C 51.00; H 3.02; Cl 21.60; S 9.73. M 329.

Oxidation of (IV) and (V). 1 g each of (IV) and (V) were heated for 5 hours with 5 g of CrO_3 in 25 ml of glacial CH_3COOH. The mixture was then poured into water. The white precipitate was recrystallized from hot alcohol. The m.p. was 251-252°. A mixed melt of the products obtained from (IV) and (V) showed no depression of the melting point. The substance turned an alcohlic solution of NaOH an intense blue color which disappeared on shaking in air.

Found %: C 50.20; H 2.10; Cl 23.00; S 9.98. $C_{13}H_6O_3Cl_2S$. Calculated %: C 49.70; H 1.92; Cl 22.60; S 10.20.

SUMMARY

1. A method was developed for obtaining the sulfonic acids of derivatives of thioxanthenol-5-dioxide by sulfonating diphenylmethane, 1,1-diphenylethane, triphenylmethane and their derivatives with 66% oleum at high temperature.

2. 3,7-Dichlorothioxanthenol-5-dioxide and 3,7-dichloro-10-methylthioxanthenol-5-dioxide were synthesized and their properties were studied.

3. The indicator properties of derivatives of thioxanthenol-5-dioxide were discovered and a structure for the colored form of these compounds was proposed.

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* Compound (IV) has acid properties. When it is heated with excess KOH in diethylene glycol the excess alkali can be back titrated and the neutralization equivalent or the molecular weight (M 320) may, therefore, be determined.

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INVESTIGATIONS IN THE FIELD OF CYANINE DYES

XI. SOME 7,7'-DIMETHYLTHIACARBOCYANINES

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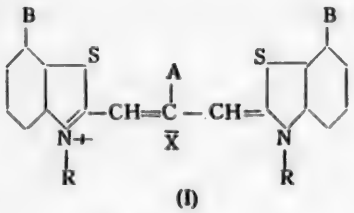
Disubstituted thiacarbocyanines with methoxy- [1], hydroxy-, acetoxy- [2], amino-, acetamino- [3] and dimethylamino-groups [4, 5] in the 7,7' positions (I) are markedly different in properties from the corresponding 4,4'-, 5,5'- and 6,6'-derivatives.

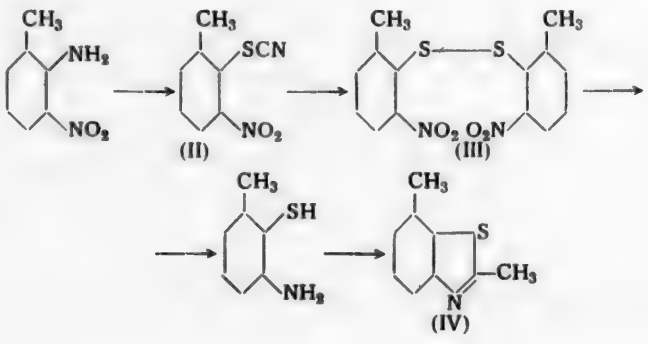


(I)

where R = alkyl, A = H or alkyl, B = substituent group, $\overline{X}$ = acid group.

Similar dyes, especially those containing an alkyl group in the meso position are generally relatively weak optical sensitizers for silver halide photographic emulsions [1, 5] and do not show a considerable capacity for sensitizing of the 2nd order [6]. The 7,7' derivatives are frequently less soluble and have higher melting points. The 7,7'-disubstituted thiacarbocyanines hitherto investigated contained groups with a considerable polarity in the heterocyclic radical. To determine the extent to which the specific properties of these dyes are connected with the electron influence of the substituents we, therefore, decided to study thiacarbocyanines with relatively neutral methyl groups in the 7,7' positions. The only dye of this type briefly mentioned in literature is 3,3'-diethyl-7,7'-dimethylthiacarbocyanine iodide [8]. It was also of interest to compare the properties of 7,7'-dimethylthiacarbocyanines and the corresponding 4,4'-, 5,5'- and 6,6'-dimethyl derivatives, which were previously obtained and investigated by A. I. Kiprianov and E. D. Sych [7].

We obtained 2,7-dimethylbenzothiazole (IV), necessary for the synthesis of 7,7'-dimethylthiacarbocyanines, from 2-amino-3-nitrotoluene according to the system



2-Thiocyanogen-3-nitrotoluene [9] (II) was obtained with an almost quantitative yield by reacting 2-nitro--6-methylphenyldiazonium sulfate with potassium thiocyanate in the presence of iron ammonium alum (comp. [10]). The disulfide (III) was obtained with the highest yields by treating the thiocyanate (II) with sodium sulfide in alcoholic solution at the usual temperature or in aqueous suspension which was boiled (comp. [11]). The 2,2'--dinitro-6,6'-dimethyldiphenyldisulfide (III) was then reduced with zinc dust in acetic acid and the 2-amino-6--methylthiophenol formed was treated, without being isolated, with acetic anhydride (comp. [1, 5, 12]). The result was the formation of 2,7-dimethylbenzothiazole (IV) with a good yield.

It was, therefore, to be assumed that 2,7-dimethylbenzothiazole can also be synthesized, possibly together with the 2,5-dimethyl derivative, by the oxidation of thioacetyl-m-toluidine with potassium ferricyanide (comp. [13]). This was in actual fact confirmed by experiment (see Experimental).* In this instance, therefore, as with the corresponding derivatives of m-anisidine [13], xylidine-(1,2,4) [14] and m-chloroaniline [15], closure of the thiazole ring occurs both in the ortho and the para position to the substituent group.

We also perfected to some extent the methods for preparing 2,4- and 2,5-dimethylbenzothiazoles, first synthesized by A. I. Kiprianov and E. D. Sych [7] (comp. also [15, 27]). It was possible to obtain the first of these compounds in a crystalline state (m.p. 33-34°).

Carbo- and dicarbocyanine dyes were obtained by condensing ethyl-p-tolusulfonates or diethyl sulfates of isomeric dimethylbenzothiazoles with ortho esters of carboxylic acids in pyridine (comp. [16]) or with the dianil of malonaldehyde (comp. [17]), respectively and were isolated in the form of the iodides, which crystallized well. By condensing these quaternary salts with p-dimethylaminobenzaldehyde (comp. [18] the corresponding 2-p-dimethylaminostyryl derivatives were also synthesized.

As has already been noted [7], 2,4-dimethylbenzothiazole forms quaternary salts with difficulty; the dyes from this base could, therefore, only be obtained with relatively low yields.

TABLE 1

Position of the methyl groups	Absorption maximum in mμ (in ethyl alcohol)					Value A of thiacarbocyanines, unsubstituted in the chain
	Carbocyanines with substituents in the 9-position			Dicarbocyanines	p-Dimethylaminostyryl derivatives	
	H	CH_3	C_2H_5			
—	558	543	547	652	529	2.80
4,4'	561a	543d	548	653	526	2.30
5,5'	565b	548e	550	656	530	2.35
6,6'	563c	548f	552	655	526	2.25
7,7'	561	547	551	653	532	3.0

Note: According to literature data the absorption maxima (in mμ) are: a) 563 [7], 565 [26]; b) 565 [26]; c) 563 [7, 26], 561 (in CH_3OH) [22]; d) 547 [7, 26]; e) 558 [7], 560 [26]; f) 550 [7].

Table 1 gives the absorption maxima of the synthesized dyes and the corresponding compounds without substituents in the heterocyclic radicals (in ethyl alcohol) and also the values of the basicity (A**) for thiacarbocyanines which are not substituted in the chain.***

The data in Table 1 show that in the case of carbo- and dicarbocyanines the introduction of methyl groups in the 5,5'- and 6,6'-positions has a much greater bathochromic influence than in the 4,4'- and 7,7'-positions.

* When this work had been completed (1952) we became acquainted with an abstract of the article by Mizuno and Adachi [15], who isolated 2,7- and 2,5-dimethylbenzothiazole from the oxidation products of thioacetyl-m--toluidine as the picrates, and also with the work of Banerdji [28] who only obtained the 2,5-dimethyl derivative by this reaction.

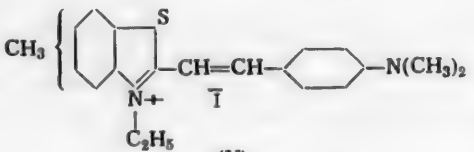
** The basicity is characterized by the value A, which is the concentration of hydrochloric acid (in moles per liter), which must be obtained in a $1 \cdot 10^{-5}$ molar solution of the dye in 57% ethyl alcohol in order to decolorize it by 50% as a result of the conversion of part of the dye to the diacid salt [19].

*** The measurements of the basicity of the dyes were made by N. S. Spasokukotsky and E. S. Kozlova, to whom we wish to express our deep appreciation.

At the same time the absorption maxima of the 4,4'- and 7,7'-dimethylthiacarbo- and dicarbocyanines, unsubstituted in the chain, on the one hand, and their corresponding 5,5'- and 6,6'-dimethyl derivatives on the other, almost completely coincide.

The same laws were found in the case of isomeric thiacarbocyanines containing more highly polar electron--donor groups (for example, CH_3O, OH, NH_2 or $N(CH_3)_2$ [1-5])in the heterocyclic radicals; the nature of the influence of these substituents and methyl groups on the color is, evidently, analogous.

It was previously established that in cyanine dyes the bathochromic influence of substituents in the heterocyclic radicals on the color is greater the more clearly their electron-donor or electron-acceptor nature is apparent [20]. Because of this fact the hypothesis was earlier advanced that in a number of thiacarbocyanines the electron displacements from the substituent groups to the polymethine chromophore are, evidently, close in the case of the 5,5'- and 6,6'-derivatives which have almost identical coloration, on the one hand, and in the case of the 4,4'- and 7,7'--disubstituted derivatives, on the other [1]. An examination of the positions of the absorption maxima of the iodoethylates of methyl-2-p-dimethylaminostyrylbenzothiazoles (V) and also of the basicity of dimethylcarbocyanines does not, however, confirm this hypothesis.



(V)

The color of styryl dyes, which have an unsymmetrical structure, depends to a large extent on the basicity of the heterocyclic radical: when the basicity is increased the uniformity of distribution of the electron density in the polymethine chromophore is reduced, as a result of which the absorption maximum is displaced into the short-wave region [22]. As may be seen from the data in Table 1, the absorption maxima of the 4- and 6-methyl--2-p-dimethylaminostyryl derivatives are considerably more displaced into the short-wave region than in the case of the unsubstituted dye, while the 5- and, in particular, the 7- methyl derivative have a rather deeper color. On the basis of these data the conclusion can be drawn that the introduction of a methyl group in the 4- and, in particular, the 6- position appreciably increases the basicity of the benzothiazole radical (the hypsochromic displacement of the absorption maximum of styryl is 3 mμ compared with the bathochromic which is 1.5 and 3 mμ, respectively, with unchanged basicity of the radical); in the 5- position the methyl group has a lesser influence on the basicity (slight bathochromic displacement) and in the 7- position it causes a certain reduction in the basicity of the heterocyclic radical (greater bathochromic displacement than the theoretical value).

The data in Table 1 also indicate that as a result of the introduction of methyl groups in various positions of the heterocyclic radicals the basicity of symmetrical thiacarbocyanine changes in the same sequence.

In contrast to certain thiazole derivatives [21], in a number of the investigated thiacarbocyanines no direct relationship is, therefore, observed between the intensification of the color as a result of the introduction of substituents and the change in the basicity of the dyes. The change in the basicity as a result of the introduction of substituent groups characterizes to a certain extent the direction and extent of the electron displacements from these substituents in the main state of the dye. It is evident, therefore, that in dimethylthiacarbocyanines and also in the above-metnioned quaternary salts of methyl-2-p-dimethylaminostyrylbenzothiazoles the electron displacements from the methyl groups in the main state of the dyes are close, but not identical, and are very different for the 5,5' and 6,6'- derivatives. Because of this,the displacement of the absorption maximum of symmetrical cyanines as a result of the introduction of substituents in their heterocyclic radical cannot completely characterize the value of the electron displacements from these groups in the main state of the dye.

The investigation of the 7,7'-dimethylthiacarbocyanines obtained showed that, like the other 7,7'-disubstituted compounds, they have a weaker sensitizing action than the corresponding isomeric dyes.

The rather specific properties of the reduced basicity of 7,7'-disubstituted thiacarbocyanines, containing electron-donating groups, is possibly associated with the formation in such dyes of two positive centers, located close to each other, on the sulfur atom and on the substituents.

We wish to express our thanks to E. B. Lifshits and K. I. Pokrovskaya who supervised the investigation of the synthesized dyes.

EXPERIMENTAL

2-Nitro-6-methylthiocyanogenbenzene. 15.2 g of 2-amino-3-nitrotoluene [23] was dissolved with heating in 70 ml of 60% sulfuric acid. After the mixture had cooled a solution of 18 g of sodium nitrite in 33 ml of water was added with stirring over a period of 10 minutes at 20-25° to the suspension of the amine sulfate obtained. The liquid was mixed for a further 20 minutes and after it had been filtered it was poured into a solution of 11 g of potassium thiocyanate and 1.66 g of iron ammonium alum in 200 ml of water at 20-25°. The next day the brown-yellow precipitate was filtered and washed with a solution of alkali and water. The yield was 19.2 g (98%), the m.p. was 37-39°. After crystallizing from ethyl alcohol light-yellow needles with an m.p. of 46-47° (45.5° [9]) were obtained.

2,2'-Dinitro-6,6'-dimethyldiphenyldisulfide. 1.46 g of 2-nitro-6-methyl-thiocyanogenbenzene was introduced into a solution of 0.48 g of crystalline sodium sulfide in 15 ml of ethyl alcohol and the mixture was shaken for 1 hour. The precipitate formed was filtered and washed with alcohol and water. The yield was 0.79 g (62%). The m.p. was 146-147° (149° after crystallizing from glacial acetic acid [9]).

2,7-Dimethylbenzothiazole. A mixture of 8.4 g of 2,2'-dinitro-6,6'-dimethyldiphenylsulfide and 17.24 g of zinc dust (100%) was introduced gradually over a period of 30 minutes with stirring into 75 ml of glacial acetic acid, heated to 80-100°. After decolorization the mass was mixed for 20 minutes at 100°. 15.3 g of acetic anhydride was then added to it and the mixture was boiled for 3 hours with a reflux condenser. After cooling to 70-80° the liquid was diluted with 50 ml of water, heated to boiling and filtered from excess zinc dust, which was washed with water and ether. A concentrated solution of 20 g of caustic soda was added to the filtrate, to which had been added the washwater and the ether; the base, which was precipitated as a yellowish mass, was steam distilled. The distillate was shaken with ether and the extract was washed with a 5% solution of caustic potash; it was then dried with potash and the ether was carefully distilled. The yield was 6.7 g (82%); the yellowish mass crystallized almost completely on cooling. To purify the base it was distilled under vacuum (b.p. 123-128° at 14 mm, b.p. 24-25°, weight 6.2 g), and then crystallized 3 times from gasoline (b.p. 60-80°).

It was in the form of colorless prisms with an m.p. of 29.5-30.5°; it was insoluble in water but very readily soluble in organic solvents (according to Banerdji [28], a light-yellow oil).

Found %: N 8.48. C_9H_9NS. Calculated %: N 8.58.

The picrate was in the form of yellow needles (from ethyl alcohol). The m.p. was 131-132° (127-129° [15], 138° [28]).

Found %: N 14.13. $C_{15}H_{12}O_7N_4S$. Calculated %: N 14.28.

The iodomethylate was obtained with a yield of 77% by heating the base for 20 hours with 2 moles of methyl iodide in a flask with a reflux condenser on a boiling water bath. After treatment with acetone during boiling the salt was crystallized twice from anhydrous ethyl alcohol. It was in the form of slightly-greenish rectangular prisms with an m.p. of 242-243°.

Found %: N 4.33, 4.46. $C_{10}H_{12}NSI$. Calculated %: N 4.59.

The iodoethylate was obtained similarly to the iodomethylate with a yield of 61% by heating the base with ethyl iodide and it was purified by treating with acetone and recrystallizing twice from anhydrous ethyl alcohol. It was in the form of colorless prisms with an m.p. of 202.5-203°.

Found %: N 4.02, 3.90. $C_{11}H_{14}NSI$. Calculated %: N 4.38.

Thioacetyl-o-toluidine. 3.97 g of phosphorus pentasulfide was added gradually over a period of 15 minutes to a boiling solution of 13.45 g of acetyl-o-toluidine in 65 ml of dry benzene, after which the mixture was boiled for 30 minutes. The solution was decanted from the tarry mass and the latter was washed with 40 ml of benzene. The benzene solutions were collected and shaken with a 5% solution of caustic soda (5 times, 50 ml each time). The alkaline solution was neutralized with acetic acid and the thioacetyl-o-toluidine was isolated as an almost colorless crystalline precipitate by passing a current of carbon dioxide. The yield was 7.3 g (49%). The m.p. was 58-59° (66° after purification [24], 42° [27]).

Thioacetyl-m-toluidine. This was obtained in a similar manner to the previous compound by boiling a solution of 7.45 g of acetyl-m-toluidine in 35 ml of dry benzene with 2.2 g of phosphorus pentasulfide for 30 minutes. The yield was 4.68 g (56%). It was in the form of almost colorless crystals with an m.p. of 59-60° (58-59° [15]; 64° after purification [24]).

2,4-Dimethylbenzothiazole. A solution of 13.2 g of thioacetyl-o-toluidine in 320 ml of 4% caustic potash was added gradually with stirring over a period of 1 hour at 0-5° to a solution of 52.8 g of potassium ferricyanide in 215 ml of water. The mixture was stirred for a further 2 hours and shaken with ether; the latter was distilled off and the residue was steam distilled. The distillate was shaken with ether, the extract was dried with potash, the ether was distilled off and the residue (7.26 g, 55%) was distilled under vacuum. The b.p. was 118-121° at 12 mm (161-163° at 55 mm [7], 128-130° at 20 mm [27]). The yield was 6.6 g (49%). It was a colorless oil; it crystallized completely on cooling. The m.p. was 30-31°. After crystallizing from gasoline it was in the form of colorless prisms with an m.p. of 33-34° (according to literature data [3], it is a liquid with an odor of pyridine).

Found %: N 8.70. C_9H_9NS. Calculated %: N 8.58.

The picrate was in the form of yellow prisms (from ethyl alcohol) with an m.p. of 147-147.5° (150-151° [27]).

Found %: N 14.27. $C_{15}H_{12}O_7N_4S$. Calculated %: N 14.28.

The iodomethylate was obtained with a yield of 11% by heating the base for 20 hours with 2 moles of methyl iodide in a flask with a reflux condenser on a boiling water bath. The quaternary salt was washed with acetone and crystallized from anhydrous ethyl alcohol. It was in the form of colorless prisms with an m.p. of 221-222°.

Found %: N 4.44. $C_{10}H_{12}NSI$. Calculated %: N 4.59.

2,5-Dimethylbenzothiazole. A mixture of 8.4 g of 2,2'-dinitro-4,4'-dimethyldiphenyldisulfide [7, 11] and 15.5 g of zinc dust (100%) was added gradually with stirring over a period of 30 minutes to 75 ml of glacial acetic acid, heated to 80-100°. After decolorization the mass was stirred for 20 minutes at 90-100°; 15.3 g of acetic anhydride was then added to it and the mixture was boiled for 4 hours with a reflux condenser. After cooling to 70-80° the mass was diluted with 125 ml of water, heated to boiling and filtered from residual zinc dust, which was washed with water and ether (the washings were added to the filtrate). After cooling, a concentrated solution of 20 g of caustic soda was added to the liquid and the yellowish mass precipitated was extracted with ether. The extract was washed with a 5% solution of caustic soda and water, dried with potash, the ether was distilled and the residue was distilled under vacuum. The b.p. was 107-108° at 6 mm. The yield was 6.1 g (74.8%). It was a colorless oil which rapidly crystallized. The m.p. was 42-43° (from gasoline)(34° [7]; according to Banerdji [28] it is a yellowish oil).

The picrate was in the form of yellow needles (from ethyl alcohol). The m.p. was 175-176° (167-168° [15]).

Oxidation of thioacetyl-m-toluidine by potassium ferricyanide. A solution of 16.5 g of thioacetyl-m-toluidine in 400 ml of a 4% solution of caustic soda was added gradually with stirring over a period of 1 hour at 0-5° to a solution of 66 g of potassium ferricyanide in 270 ml of water. The mixture was stirred for a further 2 hours and shaken with ether; the latter was distilled off and the residue was steam distilled. The base was extracted from the distillate with ether, the extract was dried with potash and the ether was distilled. The yield was 13.64 g (83.6%). It was a yellowish oil, partially crystallizing on cooling. After distillation under vacuum (126-130° at 12 mm) the yield was 76.8%. It was a colorless oil; on cooling it almost completely crystallized. 7.3 ml of gasoline was added to 18.22 g of the vacuum-distilled product, the mixture was heated until a homogeneous solution was formed and cooled. The precipitated crystals were filtered and washed with a small amount of gasoline. The yield was 3.45 g. The m.p. was 27.5-28.5°. After a second crystallization the m.p. was 29-30°; the substance showed no depression of the melting point in a mixed melt with 2,7-dimethylbenzothiazole.

The mother liquor and the gasoline washings were evaporated. The residue was distilled under vacuum. The b.p. was 128-129° at 14 mm. The weight was 12.93 g. The bases were distilled in 13 ml of alcohol and precipitated in 4 stages with picric acid (4.58 g each in 15 ml of alcohol). The picrates were washed with alcohol (5 ml) and with ether (30 ml). The total yield was 27.65 g (90%): 1st fraction 7.13 g, m.p. 159-160°; 2nd fraction 7.76 g, m.p. 123-124°; 3rd fraction 7.54 g, m.p. 125-126°; 4th fraction 5.22 g, m.p. 120-121°.

5.5 g of picrate (12%) with an m.p. of 169-172° was obtained by fractional crystallization of the 1st and 2nd fractions from ethyl alcohol. After recrystallization yellow needles with an m.p. of 175-176° were obtained;

in a mixed melt with the picrate of 2,5-dimethylbenzothiazole they showed no depression of the melting point. It was not possible to isolate the pure substance by crystallizing the 4th fraction. The picrates of the filtrates from the crystallization of the 1st and 2nd fractions were added to the picrates of the 3rd and 4th fractions. The mixture (21.04 g) was decomposed with alkali, the bases were extracted with ether, distilled under vacuum (weight 7.84 g) and crystallized from gasoline. 2.65 g of the compound with an m.p. of 27.5-28.5° was isolated. The residue (4.92 g) was not further analyzed. The total yield of 2,7-dimethylbenzothiazole was 6.1 g (33%).

Synthesis of the Dyes

To obtain the 3,3'-diethyldimethylthiacarbocyanines the corresponding bases were heated in a flask with a reflux condenser on an oil bath with a 10% excess of diethylsulfate (at 130-135° for 3 hours) or the ethyl ester of p-toluenesulfonic acid (6 hours at 140-150°). Dry pyridine and the ortho-ester of the carboxylic acid (in some instances acetic anhydride also) were added to the quaternary salt and the mixture was heated for 1 hour at 130-135° After cooling, the reaction solution was diluted with ether. The precipitate or the tarry mass formed was dissolved in ethyl alcohol with heating and the iodide of the dye was precipitated by the addition of an equal volume of a 10% potassium iodide solution. The dyes were purified by crystallizing from ethyl alcohol until a constant melting point was obtained. Table 2 gives the conditions for preparing the thiacarbocyanines, their properties and the analytical results.*

3,3'-Diethyl-4,4'-dimethylthiadicarbocyanine iodide. a) A mixture of 0.16 g of 2,4-dimethylbenzothiazole and 0.17 g of diethyl sulfate was heated for 3 hours at 130-135°. The salt was dissolved in 0.6 ml of pyridine and 0.06 g of the hydrochloride of malonaldehyde dianil and a solution of 0.11 g of piperidine in 0.4 ml of pyridine were added. After 12 hours the dye was precipitated with ether, dissolved in 10 ml of alcohol and isolated as the iodide by the addition of 10 ml of a 10% solution of potassium iodide. The yield was 0.03 g (21%). The m.p. was 219-220°.

b) The quaternary salt, obtained, as in the previous instance, from 0.16 g of base, dissolved in 2 ml of anhydrous ethyl alcohol, was added to 0.06 g of the hydrochloride of malonaldehyde dianil and a solution of 0.0025 g of sodium in 0.55 ml of anhydrous alcohol. The mixture was heated for 5 minutes on a boiling water bath and the dye was precipitated by the addition of 0.3 g of potassium iodide in 1 ml of water. The yield was 0.04 g (29%). The m.p. was 219-220°. After crystallization from alcohol it was in the form of lustrous dark-green prisms with an m.p. of 230-231°.

Found %: N 5.08, 5.10. $C_{25}H_{27}N_2S_2I$. Calculated %: N 5.12.

3,3'-Diethyl-7,7'-dimethylthiacarbocyanine iodide. 1 ml of pyridine and then 0.14 g of piperidine were added to a ground mixture of 0.32 g of the iodoethylate of 2,7-dimethylbenzothiazole and 0.13 g of the hydrochloride of malonaldehyde dianil. After 12 hours the mass was diluted with 2 ml of ethyl alcohol. The dye was filtered and washed with water and ether. The yield was 0.15 g (54%). The m.p. was 239-240°. It was in the form of lustrous green prisms (after crystallizing twice from ethyl alcohol). The m.p. was 242°.

Found %: N 5.36. $C_{25}H_{27}N_2S_2I$. Calculated %: N 5.12.

Iodoethylate of 2-p-dimethylaminostyryl-4-methylbenzothiazole. The diethyl sulfate of 2,4-dimethylbenzothiazole, obtained as before from 0.16 g of the base and 0.17 g of diethyl sulfate, was dissolved in 1 ml of anhydrous ethyl alcohol,and 0.15 g of p-dimethylaminobenzaldehyde and 0.06 g of piperidine were added. The mixture was heated for 3 hours on a boiling water bath and after cooling was diluted with ether. The precipitated dye was dissolved in alcohol (10 ml) and was converted to the iodide by the usual treatment. The yield was 0.17 g (37%). The m.p. was 207-207.5°. It was in the form of violet prisms (after crystallizing twice from ethyl alcohol). The m.p. was then 207.5-208°.

Found %: N 6.00. $C_{20}H_{23}N_2SI$. Calculated %: N 6.23.

Iodoethylate of 2-p-dimethylaminostyryl-5-methylbenzothiazole. 0.48 g of 2,5-dimethylbenzothiazole and 0.66 g of ethyl p-toluenesulfonate were heated for 6 hours at 145-150°. 0.45 g of the p-dimethylbenzaldehyde, 4 ml of anhydrous ethyl alcohol and 0.18 g of pyridine were added to the crystalline mass obtained and the mixture was heated for 3 hours on a boiling water bath. The solution was diluted with ether, the precipitate formed was

* Before analysis all the compounds were dried at 60-90° under vacuum over phosphorus pentoxide.

TABLE 2

Name of the dye	Amount of base (in g)	Amount of $(C_2H_5)_2SO$ (I) or $p\text{-}C_7H_7SO_2C_2H_5$ (II) (in g)	Ortho-ester and its amount (in g)*	Amount of pyridine (in ml)	Yield (as %)	External appearance	Melting point	Found		Calculated		
								Element	Content (as %)	Formula	Element	Content (as %)
3,3'-Diethyl-4,4'-dimethylthiacarbocyanine iodide [7, 26]	0.32	I—0.34	III—0.45	3.0	48	Blue-violet needles	246–247° (254° [26])	N	5.16 5.22	$C_{23}H_{25}N_2S_2I$	N	5.38
3,3'-Diethyl-4,4',9-trimethylthiacarbocyanine iodide [7, 26]	0.32	I—0.34	IV—0.32 **	3.0	9	Reddish-brown needles	228—229	N	5.35	$C_{24}H_{27}N_2S_2I$	N	5.24
3,3',9-Triethyl-4,4'-dimethylthiacarbocyanine iodide.	0.32	I—0.34	V—0.26 **	3.0	5.5	Lustrous brown prisms	224—225	N	5.16	$C_{25}H_{29}N_2S_2I$	N	5.11
3,3'-Diethyl-5,5'-dimethylthiacarbocyanine iodide [7, 26]	0.32	II—0.44	III—0.45	2.0	82	Blue needles with bronze shade	268—270 (277° [26])					
3,3'-Diethyl-5,5',9-trimethylthiacarbocyanine iodide [7, 26]	0.32	II—0.44	IV—0.49	2.0	50.6	Fine brownish-red prisms	278—280 (282° [26])					
3,3',9-Triethyl-5,5'-dimethylthia carbocyanine iodide.	0.32	II—0.44	V—0.53	2.0	54.7	Lustrous blue prisms	251—252	I	23.45	$C_{25}H_{29}N_2S_2I$	I	23.15
3,3'-Diethyl-6,6'-dimethylthiacarbocyanine iodide [7, 22, 25].	0.32	II—0.44	III—0.59	2.0	59.6	Blue-green prisms	285—287 (285° [25], 281° [26])	I	24.21	$C_{23}H_{25}N_2S_2I$	I	24.40
3,3'-Diethyl-6,6',9-trimethylthiacarbocyanine iodide [7, 26].	0.32	II—0.44	IV—0.64	2.0	40.6	Violet needles (from CH_3OH)	265—266 (275° [26])	I	23.52	$C_{24}H_{27}N_2S_2I$	I	23.76
3,3',9-Triethyl-6,6'-dimethylthiacarbocyanine iodide.	0.32	II—0.44	V—0.74	2.0	40	Lustrous blue prisms	255	I	23.37	$C_{25}H_{29}N_2S_2I$	I	23.15
3,3'-Diethyl-7,7'-dimethylthiacarbocyanine iodide [8].	0.32	II—0.44	III—0.45	3.0	84	Greenish-brown prisms with golden luster	283—284 (~300° [8])	N	5.26	$C_{23}H_{25}N_2S_2I$	N	5.38
3,3'-Diethyl-7,7',9-trimethylthiacarbocyanine iodide.	0.32	II—0.44	IV—0.50	3.0	52	Violet needles	291—292	N	5.21	$C_{24}H_{27}N_2S_2I$	N	5.24
3,3',9-Triethyl-7,7'-dimethylthiacarbocyanine iodide.	0.32	II—0.44	V—0.53	3.0	40	Brown prisms with golden luster.	272—273	N	5.00	$C_{25}H_{29}N_2S_2I$	N	5.11

* III — Ethyl orthoformate, IV — ethyl orthoacetate, V — ethyl orthopropionate.

** 0.05 g of acetic anhydride added.

washed several times with ether, dissolved with heating in 60 ml of alcohol and the iodide of the dye was precipitated by the addition of a 10% solution of potassium iodide (60 ml). The precipitate was filtered and washed with water and alcohol. The yield was 1.17 g (86.8%). The m.p. was 242-243° (with decomp.). After crystallizing from 65 parts of ethyl alcohol it was in the form of lustrous red prisms with an m.p. of 251-252° (with decomp.).

Found %: N 6.13. $C_{20}H_{23}N_2SI$. Calculated %: N 6.23.

Iodoethylate of 2-p-dimethylaminostyryl-6-methylbenzothiazole. This was obtained in a similar manner from the ethyl-p-toluenesulfonate of 2,6-dimethylbenzothiazole (obtained from 0.48 g of base). To isolate the iodide of the dye 10 ml of a 20% solution of potassium iodide was added to a solution of the p-toluenesulfonate in 75 ml of alcohol. The yield was 1.1 g (81.6%). The m.p. was 274-275° (with decomp.). It was in the form of lustrous violet prisms (from 235 parts of ethyl alcohol). The m.p. was 282-283° (with decomp.) (286-287° [22]).

Found %: N 6.10. $C_{20}H_{23}N_2SI$. Calculated %: N 6.23.

Ethylethyl sulfate of 2-p-dimethylaminostyryl-7-methylbenzothiazole. The diethyl sulfate of 2,7-dimethylbenzothiazole, obtained by heating 0.16 g of the base with 0.17 g of diethylsulfate for 3 hours at 130-135°, was dissolved in 1 ml of anhydrous ethyl alcohol, and 0.15 g of p-dimethylaminobenzaldehyde and 0.03 g of piperidine were added. The mixture was heated for 3 hours on a boiling water bath. The dye which precipitated out from the hot solution was filtered after cooling and washed with water, alcohol and ether. The yield was 0.29 g (64.7%). The m.p. was 240-241°. After crystallizing twice from alcohol it was in the form of red rectangular prisms with an m.p. of 242-242.5°.

Found %: N 6.02. $C_{22}H_{28}O_4N_2S_2$. Calculated %: N 6.25.

The absorption curves of the dyes were determined in a $1 \cdot 10^{-4}$ mole alcoholic solution in an SF-4 spectrophotometer.

SUMMARY

1. 2,7-Dimethylbenzothiazole was synthesized; a number of carbo- and dicarbocyanines and 2-p-dimethylaminostyryl derivatives were obtained from the quaternary salts of this base and other dimethylbenzothiazoles.

It was shown that by oxidizing thioacetyl-m-toluidine with potassium ferricyanide a mixture of 2,7- and 2,5-dimethylbenzothiazoles is formed.

2. It was shown that the introduction of methyl groups in the heterocyclic radical of thiacarbocyanines has a practically equal bathochromic effect in the 4,4'- and 7,7'-positions, on the one hand, and in the 5,5'- and 6,6'-positions, on the other. The presence of these groups in these positions exerts a different influence, however, on the basicity of the dyes and the benzothiazole group.

Because of this the change in the color of thiacarbocyanines resulting from the introduction of substituents in the heterocyclic groups cannot, evidently, completely characterize the value of the electron displacement from these groups in the main state of the dye.

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INVESTIGATION IN THE FIELD OF SYNTHESIS AND CONVERSIONS IN THE SERIES OF DIARYL UREAS

IV. SYNTHESIS OF DIARYL UREAS, SUBSTITUTED IN THE RING BY HALOIDS AND OTHER SUBSTITUENTS

D. F. Kutepov and N. S. Rozanova

We have previously described the preparation of the three isomers of hexachlorodiphenyl urea, and also 2,2',4,4',5,5'-hexafluorodiphenyl urea. In order to compare the chemical properties of these compounds we also prepared and studied 2,2',4,4',6,6'-hexabromodiphenyl urea. This compound was synthesized by the phosgenation of 2,4,6-tribromoaniline which in turn was obtained by the bromination of aniline [1]. The phosgenation of tribromoaniline was carried out in a medium of nitrobenzene at 130°.

The study of the properties of diaryl ureas containing halogen and a polar group, for example, a nitro group in the ring simultaneously was of interest. Compounds of this type have not been described in literature. We synthesized 2,2',6,6'-tetrachloro-4,4'-dinitrodiphenyl urea and 2,2',4,4'-tetrafluoro-6,6'-dinitrodiphenyl urea. It is characteristic that the reaction of dihalogennitroanilines with phosgene does not lead to the formation of the corresponding diaryl ureas (both in an aqueous-dichloroethane medium in the presence of roasted alkali and OP-7 emulsifier and in a medium of nitrobenzene at 135°). We only succeeded in obtaining 2,2',6,6'-tetrachloro-4,4'-dinitrodiphenyl urea by the phosgenation of 2,6-dichloro-4-nitroaniline in toluene solution in sealed ampoules at 150°.

We obtained 2,2',4,4'-tetrachloro-6,6'-dinitrodiphenyl urea with a very negligible yield by the phosgenation of 2,4-difluoro-6-nitroaniline in a medium of trichlorobenzene in sealed tubes at 85-90°. The initial difluoronitroaniline was obtained by the nitration of 4-acetylamino-1,3-difluorobenzene with nitrosyl sulfuric acid by Finger's method [2]. Attempts to obtain tetrafluorodinitrodiphenyl urea by the phosgenation of 2,4-difluoro-6-nitroaniline in a medium of dichloroethane in the presence of alkali at room temperature, in an aqueous medium without an alkaline agent, in nitrobenzene at 130°, and also by condensing difluoronitroaniline with urea in a medium of isoamyl alcohol [3] and dichloroethane did not give the desired results. In all instances the unchanged initial difluoronitroaniline was obtained.

The conclusion may, therefore, be drawn that anilines having halogens and a nitro group as substituents in the ring simultaneously react far more difficultly with phosgene than those containing only halogens. To obtain the corresponding diaryl ureas requires more rigorous conditions — phosgenation under pressure in a sealed tube at an increased temperature.

EXPERIMENTAL

2,2',4,4',6,6'-Hexabromodiphenyl urea. 123 g of tribromoaniline and 400 ml of nitrobenzene were introduced into a reaction vessel equipped with a stirrer, reflux condenser, thermometer and a bubbler. The mixture was heated at 130° for 30 minutes, the tribromoaniline passing into solution. An excess of phosgene was passed into the solution at this temperature for 2 hours. After maintaining the mixture at this temperature for 2 hours it was allowed to stand overnight. The precipitate which formed was filtered and washed with nitrobenzene and carbon tetrachloride. The 2,2',4,4',6,6'-hexabromodiphenyl urea obtained melted at 317.5° (according to literature data, 320°).

Found %: C 23.74, 23.65; H 0.86, 0.83; N 4.58, 4.34; Br 71.01, 70.75. $C_{13}H_6ON_2Br_6$. Calculated %: C 22.75; H 0.87; N 4.09; Br 69.94.

2,2',6,6'-Tetrachloro-4,4'-dinitrodiphenyl urea. 10 ml of toluene, 0.5 g of phosgene and 2 g of 2,6-dichloro--4-nitroaniline were introduced into a hard-glass tube. The ampoule was sealed after which it was heated on an oil bath for 8 hours at 150°. After this period the tube was opened and the precipitate contained in it was extracted and treated with acetone in order to dissolve the unreacted dichloronitroaniline. The 2,2',6,6'-tetrachloro-4,4'--dinitrodiphenyl urea purified in this way melted at 250-251°. The yield was 11%. The compound was obtained for the first time.

Found %: C 35.55, 35.56; N 12.19, 12.34; Cl 32.24. $C_{13}H_6O_5N_4Cl_4$. Calculated %: C 35.45; N 12.72; Cl 32.22.

2,2',4,4'-Tetrafluoro-6,6'-dinitrodiphenyl urea. 1. The preparation of 4-acetylamino-1,3-difluorobenzene. 13 g of acetic anhydride was added dropwise to an aqueous emulsion of 15 g of m-difluorobenzene with stirring and at 0°. The precipitate formed was filtered and washed with water. After recrystallization from ethyl alcohol the acetyl derivative obtained in this way melted at 121° (according to literature data, 120.9°).

2. The preparation of 2,4-difluoro-6-nitroaniline. 20 g of the acetyl derivative, 24 ml of concentrated sulfuric acid and 8 ml of glacial acetic acid were placed in a reaction vessel. The contents of the latter were mixed until the solid material dissolved; after the solution obtained had cooled to 20° a mixture of 185 ml of concentrated nitric acid (d 1.5) and 185 ml of concentrated sulfuric acid was added to it over a period of 15 minutes. The reaction mass was heated to 40-50° and stirring was continued at this temperature for a further 1.5 hours, after which the mixture was poured on to ice. The 2,4-difluoro-6-nitroacetylaminobenzene was hydrolyzed by heating for 2 hours with concentrated sulfuric acid on a boiling water bath. The mixture was poured on to ice and the difluorodinitroaniline was steam distilled; the b.p. of the 2,4-difluoro-6-nitroaniline was 85.5-86.5°.

We succeeded in obtaining 2,2',4,4'-tetrafluoro-6,6'-dinitrodiphenyl urea by reacting difluoronitroaniline with phosgene in sealed tubes in a medium of trichlorobenzene, the mixture being heated to 85-90° for 3 hours. The yield was only 1.8%. The product melted at 232°. This compound was obtained for the first time and is not described in literature.

Found %: C 40.98, 40.52; N 15.10, 15.06. $C_{13}H_6O_5N_4F_4$. Calculated %: C 41.71; N 14.97.

SUMMARY

1. Diaryl ureas, substituted in the ring by both halogen and other substituents simultaneously, were synthesized.

2,2',6,6'-Tetrachloro-4,4'-dinitrodiphenyl urea and 2,2',4,4'-tetrafluoro-6,6'-dinitrodiphenyl urea were obtained for the first time.

2. It was shown that anilines having both halogen and a nitro group as substituents in the ring simultaneously react difficultly with phosgene and rigorous conditions are required to obtain the corresponding diaryl ureas.

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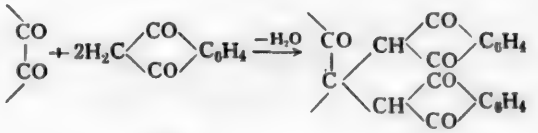
COMPOUNDS WITH TWO HEMIN INDANDIONE GROUPS IN THE MOLECULE

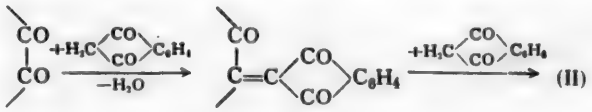
L. S. Geita and G. Ya. Vanags

When investigating the reaction of indan-1,3-dione (I) with phenanthrenequinone and acenaphthenequinone [1-4] we established that one carbonyl group of these quinones condenses with 2 molecules of indandione, with the splitting off of 1 molecule of water and the formation of a diindandionyl derivative (II).



(I) (II)

The mechanism of this reaction was also explained. It was found that first 1 molecule of quinone condenses with 1 molecule of indandione with the formation of an indandionylene derivative (III); the latter immediately adds a second molecule of indandione at its active double bond with the formation of a diindandionyl derivative.

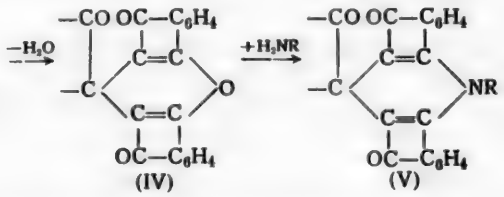


(III)

Under specific conditions the diindandionyl derivative, in turn, again easily splits off a molecule of indandione and is converted again to an indandionylene derivative. Depending on the conditions the reaction can, therefore, proceed in both directions (III $\rightleftharpoons$ II).

The compounds of type (II) obtained, containing two indandione groups at one carbon atom, show certain interesting properties. For example, they are converted by dehydrating agents to the corresponding pyrans (IV), while the latter are converted by the action of ammonia or amines to dihydropyridines (V).

In the dienol form (II)

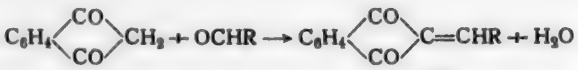


(IV) (V)

Therefore, proceeding from the easily obtainable indandione and quinones we simply pass to the complex heterocyclic compounds, derivatives of pyran and pyridine.

It was of interest to investigate whether hemin diindandione derivatives containing simpler radicals instead of a phenanthrene or acenaphthene group would behave in a similar manner. We devised the following method

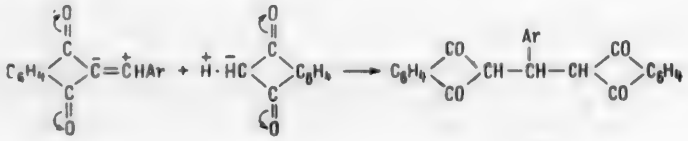
for obtaining the corresponding derivatives. It is known that indandione easily condenses with aldehydes, especially aromatic ones [5-9], according to the general system



(VI)

The arylideneindandiones obtained (VI) are in essence compounds of type (III) and it was, therefore, to be expected that they would add a second molecule of indandione. Experiments are described in literature on the addition of malonic ester [10], desoxybenzoin [11], dimedone and indandione [12] to the active double bond of arylideneindandiones. Positive results were obtained with the first two compounds. Jonescu tried to add indandione as well to arylideneindandiones [12] by boiling both components in an alcoholic solution in the presence of piperidine, although indications had previously been obtained [13] that under these conditions indandione is readily converted to bindone. Instead of a primary addition product – benzylidenebisindandione (VII) – Jonescu obtained, therefore, a condensation product of bindone and benzalindandione. Jonescu finally obtained benzylidenebisindandione by an indirect method, by the action of indandione on the condensation product of benzalindandione with desoxybenzoin, the expected benzylidenebisindandione being formed in the exchange reaction [14].

When studying the systematic addition of indandione to various arylideneindandiones we found that this reaction often takes place just as readily as with additions of type (III). For example, benzalindandione with indandione readily gives benzylidenebisindandione or phenyldiindanionylmethane (VII).



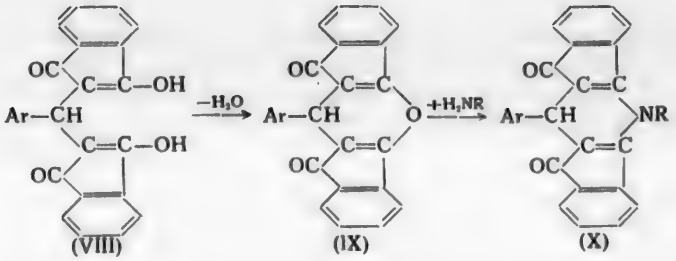
VII

o- and p-nitrobenzalindandiones add indandione still more readily, with the formation of the corresponding diindandionyl derivatives (VII, Ar = $C_6H_4NO_2$). The latter may also be obtained directly by heating the corresponding aldehyde with two molecules of indandione, the formation of arylidenedione and the addition of a second molecule of indandione taking place in succession. Indandione adds already-prepared m-nitrobenzalindandione with rather more difficulty and the corresponding diindandionyl derivative is better obtained by the indirect condensation of m-nitrobenzaldehyde with 2 molecules of indandione.

Attempts to add indandione to arylideneindandiones containing a hydroxy-, methoxy- or amino group were unsuccessful. The experiments were carried out with o-hydroxybenzal-, anisal, 3-methoxy-4-hydroxybenzal-, piperonal- and p-dimethylaminobenzal-indandione. Addition did not take place even when catalysts (piperidine, hydrochloric acid) were used. Either the unchanged reaction products or, in some instances, bindone were obtained. Diindandionyl derivatives were also not obtained by condensing hydroxy-, methoxy- or dimethylaminobenzaldehyde with excess indandione.

The experiments carried out indicate that the electrophilic substituents in arylideneindandiones, by drawing off electrons from the ethylene bond, assist the addition of indandione at this double bond; nucleophylic substituents on the other hand impede this addition. A similar influence of substituents on the condensation reaction of benzaldehydes [15] and also on the capacity of arylideneindandiones to addition reactions [10] has been mentioned in literature.

Similarly to the previously investigated diindandionyl-phenanthrones and acenaphthenones, under the influence of acetic anhydride in the presence of concentrated sulfuric acid the arylideneindandionylmethanes also split off a molecule of water from their enol forms (VIII) and give the corresponding pyrans (IX). Under the influence of amines the latter can be converted to the corresponding dihydropyridines (X).



We recently showed [16] that the main substance of this group – diindandionylmethane (VII, Ar = H) – also readily undergoes ring closure with the formation of dibenzoylenepyran. The cyclization of hemin diindandionyl derivatives into the corresponding pyrans is, therefore, one method of obtaining these compounds.

EXPERIMENTAL

We generally obtained the arylideneindandiones, required in this work as initial compounds, by heating indandione and the corresponding aldehyde in acetic acid with the addition of several drops of concentrated sulfuric or hydrochloric acid. The arylideneindandiones were obtained in a purer state than when piperidine was used as a catalyst.

Example. Benzalindandione (VI, R = C_6H_5). 1) 2.75 g of indandione, 2 g of benzaldehyde and 10 ml of glacial acetic acid were heated to boiling, 3 drops of concentrated sulfuric acid were added and the mixture allowed to stand. The next day the precipitated crystals of benzaldehyde were separated and washed with alcohol. The yield was 3.2 g (72.5%), the m.p. was 152°.

2) 4.1 g of indandione was dissolved with heating in 10 ml of glacial acetic acid, 3 g of benzaldehyde and 3 drops of concentrated hydrochloric acid were added and the mixture was heated on a water bath for 30 minutes. After cooling, the precipitated crystals were separated and washed with alcohol. The yield was 4.5 g (68.4%) of benzalindandione, the m.p. was 152°.

Phenyldiindandionylmethane (VII, Ar = C_6H_5). 1) 3 g of benzalindandione, 1.86 g of indandione and 30 ml of alcohol were boiled for 20 minutes. The initial substances passed into solution and phenyldiindandionylmethane was precipitated as fine colorless crystals. After cooling for half an hour the crystals were separated and washed with alcohol. The yield was 4.2 g (86.2%), the m.p. was 159-160°; after crystallization from chloroform with the addition of alcohol the m.p. was 160-161°. It dissolved in concentrated sulfuric acid producing a dark-red color which gradually changed to yellow; it dissolved in alkali producing an orange color. It was readily soluble in chloroform, even in the cold, and dissolved with heating in glacial acetic acid, acetone, benzene, alcohol and carbon tetrachloride.

Found %: C 79.03; H 4.13. $C_{25}H_{16}O_4$. Calculated %: C 78.94; H 4.21.

2) 2.75 g of indandione, 30 ml of alcohol and 1 g of benzaldehyde were heated on a water bath for 1 hour. Fine colorless crystals were precipitated. These were washed with alcohol and ether. The yield was 2 g of phenyldiindandionylmethane containing a small amount of some yellow admixture. After crystallization from a mixture of chloroform and alcohol it was in the form of colorless crystals with an m.p. of 160-160.5°.

Found %: C 79.38; H 4.58. $C_{25}H_{16}O_4$. Calculated %: C 78.94; H 4.21.

Phenyldibenzoylenepyran (IX, Ar = C_6H_5). 1 g of phenyldiindandionylmethane was dissolved with heating in 5 ml of acetic anhydride, 2 drops of concentrated sulfuric acid were added and the mixture was heated to boiling which was continued for 30 minutes on a water bath. Crystals of phenyldibenzoylenepyran were precipitated as fine yellow rectangular platelets. These were washed with acetic acid and alcohol. The yield was 0.8 g (84%), the m.p. was 290°. It did not dissolve in dilute alkali but was soluble in concentrated sulfuric acid, giving a brown color. It was readily soluble in chloroform and also dissolved in acetone, benzene, glacial acetic acid and carbon tetrachloride; it was not very soluble in alcohol.

Found %: C 83.10, 82.77; H 4.16, 3.98. $C_{25}H_{14}O_3$. Calculated %: C 82.87, H 3.87.

p-Nitrophenyldiindandionylmethane (VII, Ar = p-$C_6H_4NO_2$). 1) 0.35 g of p-nitrobenzalindandione, 0.2 g

of indandione and 50 ml of alcohol were boiled for 4 hours. The initial substances gradually dissolved and fine colorless crystals of p-nitrophenyldiindandionylmethane were precipitated. The yield was 0.44 g (82.7%), the m.p. was 190-193°. It dissolved in concentrated sulfuric acid giving a dark-red color, and in alkali giving a red color. It was soluble in chloroform and glacial acetic acid but was only slightly soluble in alcohol, acetone and benzene.

Found %: N 3.43. $C_{25}H_{15}O_6N$. Calculated %: N 3.29.

2) 2 g of indandione was added to 1 g of p-nitrobenzaldehyde and the mixture was boiled for 30 minutes. Colorless crystals of p-nitrophenyldiindandionylmethane were precipitated from the dark-red solution. The yield was 2.3 g (82.4%), the m.p. was 190-193°.

Found %: N 3.16. $C_{25}H_{15}O_6N$. Calculated %: N 3.29.

p-Nitrophenyldibenzoylenepyran (IX, Ar = p-$C_6H_4NO_2$). 1.25 g of p-nitrophenyldiindandionylmethane was dissolved with heating in 5 ml of acetic anhydride, 2 drops of concentrated sulfuric acid were added, the mixture was boiled and then heated for 1 hour on a water bath. The precipitated yellow crystalline platelets of p-nitrophenyldibenzoylenepyran were washed with acetic acid and alcohol. The yield was 1.1 g (91.9%), the m.p. was 287°. It did not dissolve in alkali but was soluble in concentrated sulfuric acid giving a dark-brown color. It was soluble in chloroform and glacial acetic acid but was difficultly soluble in benzene, acetone, carbon tetrachloride and alcohol.

Found %: N 3.66. $C_{25}H_{13}O_5N$. Calculated %: N 3.44

o-Nitrophenyldiindandionylmethane (VII, Ar = o-$C_6H_4NO_2$). 1) 1 g of o-nitrobenzalindandione, 0.5 g of indandione and 20 ml of alcohol were boiled for 1 hour. The yield was 1.2 g (79.4%) of pink crystals of o-nitrophenyldiindandionylmethane, the m.p. was 191-191.5°. It was soluble, producing a red color, both in concentrated sulfuric acid and in alkalis. It was soluble in chloroform and in acetic anhydride and difficultly soluble in acetone, benzene and glacial acetic acid; it was almost insoluble in alcohol and carbon tetrachloride.

Found %: N 3.52. $C_{25}H_{15}O_6N$. Calculated %: N 3.29.

2) 2 g of o-nitrobenzaldehyde, 4 g of indandione and 20 ml of alcohol were boiled for 30 minutes. The yield was 4.6 g (81.7%) of pink crystals of o-nitrophenyldiindandionylmethane, the m.p. was 191°.

Found %: N 3.48. $C_{25}H_{15}O_6N$. Calculated %: N 3.29.

o-Nitrophenyldibenzoylenepyran (IX, Ar = o-$C_6H_4NO_2$). This was prepared similarly to p-nitrophenyldibenzoylenepyran. The yield was 67.9%, the m.p. was 288°. It dissolved in concentrated sulfuric acid giving a red-brown color. It was difficultly soluble in the usual organic solvents.

Found %: N 3.52. $C_{25}H_{13}O_5N$. Calculated %: N 3.44.

m-Nitrophenyldiindandionylmethane (VII, Ar = m-$C_6H_4NO_2$). 1 g of m-nitrobenzaldehyde, 2 g of indandione and 15 ml of alcohol were boiled for 1 hour. Fine colorless crystals of m-nitrophenyldiindandionylmethane were precipitated from the dark solution. The hot solution was filtered. The yield was 2.3 g (82.4%), the m.p. was 179° (with decomp.). It dissolved in dilute alkali giving an orange-red color, and in concentrated sulfuric acid giving a red color. It dissolved in chloroform in the cold. When boiled in organic solvents – glacial acetic acid, benzene, acetone, alcohol, chloroform – the substance dissolved but yellow crystals of m-nitrobenzalindandione were precipitated from the solution instead of the reprecipitation of colorless m-nitrophenyldiindandionylmethane. It is clear, therefore, that a pure product is not obtained by the method of the addition of indandione to nitrobenzalindandione because an equilibrium of the type (III) ⇌ (II) is established.

Found %: N 3.53. $C_{25}H_{15}O_6N$. Calculated %: N 3.29.

m-Nitrophenyldibenzoylenepyran (IX, Ar = m-$C_6H_4NO_2$). This was prepared in a similar manner to p-nitrophenyldibenzoylenepyran. The yield was 91.7%, the m.p. was 280°. It was insoluble in alcohol and glacial acetic acid but was slightly soluble with heating in chloroform, benzene, carbon tetrachloride and acetone.

Found %: N 3.51. $C_{25}H_{13}O_5N$. Calculated %: N 3.44.

N-Phenyl-4-m-nitrophenyldibenzoylenedihydropyridine (X, Ar = m-$C_6H_4NO_2$; R = C_6H_5). 0.5 g of m-nitrophenyldibenzoylenepyran, 10 ml of pyridine and 1.5 ml of aniline were heated on a water bath for 4.5 hours. 15 ml

of glacial acetic acid was added to the filtrate and the mixture was heated on the water bath for 1 hour. Dark-red crystals of N-phenyl-4-m-nitrophenyldibenzoylenedihydropyran separated out the following day. The yield was 0.2 g, the m.p. was 260°. It was not soluble in alkalis but dissolved in concentrated sulfuric acid giving a green color. It was soluble in the cold in chloroform, benzene and acetone and in glacial acetic acid, alcohol and carbon tetrachloride with heating.

Found %: N 6.13. $C_{31}H_{18}O_4N_2$. Calculated %: N 5.81.

SUMMARY

Benzalindandione and nitrobenzalindandione add indandione at the position of the active double bond and form compounds containing two indandione groups at one carbon atom. Benzalindandione containing nucleophilic substituents in the arylidene group do not add indandione.

By the action of acetic anhydride in the presence of concentrated sulfuric acid, hemin diindandionyl compounds split off a molecule of water from both enol hydroxyl groups and are converted to derivatives of pyran. Under the influence of aniline these derivatives replace the oxygen bridge by nitrogen and give the corresponding N-phenyl derivatives of dihydropiperidine.

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THE SYNTHESIS OF CERTAIN AMINO- AND NITRO DERIVATIVES OF BIPHENYL, CONTAINING 2,2'-DIMETHOXY AND 3,3'-DIMETHYL GROUPS

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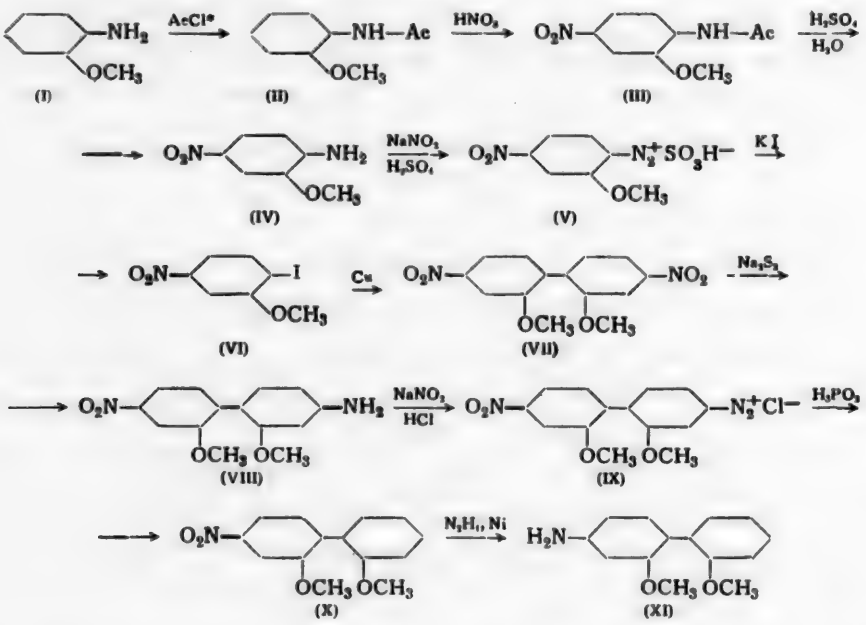
For the kinetic investigations being carried out in our laboratory it was necessary to prepare 2,2'-dimethoxy and 3,3'-dimethyl derivatives of 4-aminobiphenyl and 4-amino-4'-nitrobiphenyl.

We found that the synthesis of the methoxy derivatives was best carried out according to system 1.

System 1



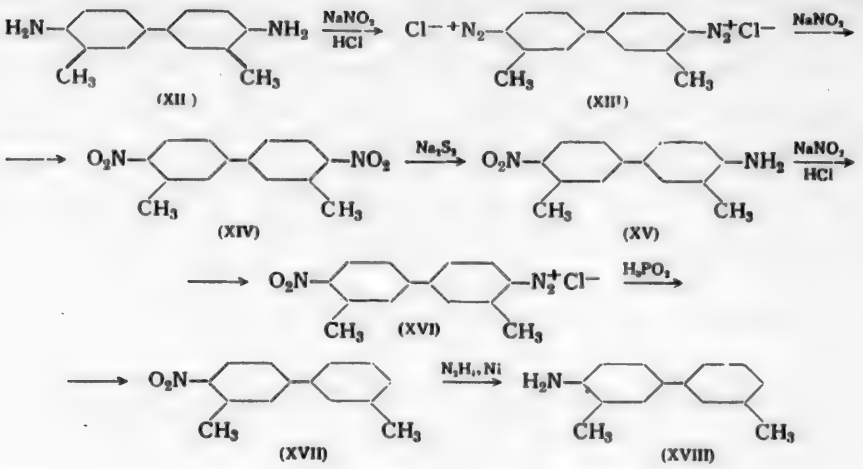
(I) (II) (III) (IV) (V) (VI) (VII) (VIII) (IX) (X) (XI)

4-Amino-4'-nitro-2,2'-dimethoxybiphenyl (VIII) and 4-amino-2,2'-dimethoxybiphenyl (XI) have not been described in literature. As regards the intermediate product — 4,4'-dinitro-2,2'-dimethoxybiphenyl (VII) — we found only an abstract [1] of a work, which we were quite unable to obtain, in which this compound is only mentioned without any indication of its method of preparation or any of its characteristics. The other intermediate product — 4-nitro-2,2'-dimethoxybiphenyl (X) was also unknown.

The initial substance for preparing the methyl derivatives was the readily available o-tolidine (XII). The synthesis was carried out according to system 2.

* Ac is the acyl group ($C_6H_5SO_2$ or p-$CH_3C_6H_4SO_2$).

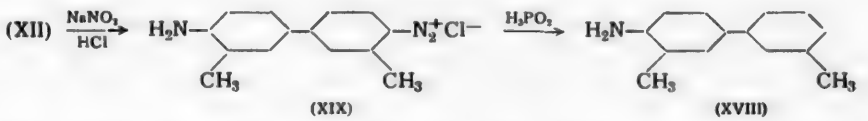
System 2



4-Nitro-3,3'-dimethylbiphenyl (XVII) and 4-amino-3,3'-dimethylbiphenyl (XVIII) have also not hitherto been described in literature.

We also synthesized the amine (XVIII) by a more direct method, i.e., by the partial deamidization of the o-tolidine itself. The reactions occurring in this instance are represented in system III.

System 3



In this system mention must be made of the stage of the partial diazotization of the o-tolidine. The possibility of a similar reaction for aromatic diamines was indicated by Tauber [2], as far back as 1894, from the example of benzidine. This reaction was subsequently used for replacing an amino group in benzidine by other substituents (see, for example, [3]). This work shows that the 3,3'-alkyl derivatives of benzidine may also be subjected to similar conversions.

Although the method of preparing the amine (XVIII) by system 3 is the most convenient it is very useful to carry out system 2 because the synthesis of this amine by completely different methods is the best means of proving its structure; system 2, in particular, which has already received adequate approval is especially conclusive in this respect.

EXPERIMENTAL

I. Synthesis of 4-Amino-4'-nitro-2,2'-dimethoxybiphenyl and 4-Amino-2,2'-dimethoxybiphenyl

a) N-(2-Methoxyphenyl)-benzenesulfamide (II). 190 g of o-anisidine was suspended by means of a mechanical stirrer in 920 ml of water, and 380 ml of benzenesulfonylchloride was poured in a continuous stream into this mixture. The temperature of the reaction mass was brought by gradual heating (20-30 minutes) to 50-55°. Without discontinuing stirring, 140 g of anhydrous soda was then added, care being taken to avoid frothing. After all the soda had been added stirring was continued for a further 2.5-3 hours at the same temperature. The mixture was allowed to cool without the stirrer being switched off and the crystalline mass which was in the form of small lumps was filtered and washed with water. The reaction product was dissolved in a large amount of hot 2% caustic soda solution (not more than 50-60°), the alkaline solution was treated with activated carbon at the same temperature and the acyl derivative was precipitated with hydrochloric acid. The yield was 400 g (98%), the m.p. was 88-89°,

which corresponds to literature data [5]. If p-toluenesulfonylchloride is used instead of benzenesulfonylchloride for the acylation the result obtained is equally good.

We used the method described for the synthesis of acyl derivatives of o-anisidine (recommended to us by V. L. Plakidiny) with success for the acylation of a number of other aromatic amines by these acyl chlorides.

b) N-(2-Methoxy-4-nitrophenyl)-benzenesulfonamide (III). 800 g of the finely ground benzenesulfonyl-derivative of o-anisidine was added gradually with vigorous mechanical stirring to 3750 ml of 10% nitric acid and the mixture was gradually heated to 90-95° on a water bath. Stirring was continued at this temperature for 6.5-7 hours. The suspension obtained was cooled and the crystals of the nitro compound were filtered and washed with water. The yield was 900 g (96%), the m.p. was 175-177°; after recrystallization from pyridine it was increased to 180-181°, which corresponds to literature data [6]. The uncrystallized product was, however, completely suitable for the next synthetic operation.

We also nitrated o-anisidine p-toluenesulfonate under identical conditions and obtained perfectly similar results (comp. [7]).

c) 2-Methoxy-4-nitroaniline (IV). 1080 g of 2-methoxy-4-nitroaniline benzenesulfonate was mixed with 1700 ml of 90% sulfuric acid and the entire mass was heated to 50-60°, complete solution of the solid particles being obtained by trituration. After being kept at this temperature for 50 minutes the liquid was decanted into not less than 10 times the amount of cold water. The mixture was made alkaline with ammonia and the crystalline amine was filtered, washed with water and recrystallized from methyl alcohol. The yield was 410 g, the m.p. was 139° (139-140° [6]). A further 50 g of a less pure product was obtained from the methanolic mother liquor (total yield 78%).

When the corresponding p-toluenesulfonate was saponified, with the same ratios of the reagents being employed, it was necessary to continue the reaction for 2 hours at 25-30°.

d) 2-Methoxy-4-nitroiodobenzene (VI). 60 g of finely-ground 2-methoxy-4-nitroaniline was suspended in a mixture of 600 ml of water and 200 ml of concentrated sulfuric acid, cooled to +8-10°. A solution of 25 g of sodium nitrite in 100 ml of water was added dropwise to this suspension which was vigorously stirred with a mechanical stirrer. After all the nitrite had been added stirring was continued until all the solid particles had dissolved, 20-30 minutes usually being required for this purpose. The filtered diazo solution was slowly added to a solution consisting of 120 g of potassium iodide and 60 g of iodine (comp. [4]) in 120 ml of water and the mixture was then heated for 1 hour on a boiling water bath. After the free iodine had been decomposed with sodium bisulfite (heating until decolorization) the mixture was cooled and the crystalline precipitate of the iodo derivative was filtered and washed with water. The yield was about 100 g (100%). After recrystallization from methyl alcohol the m.p. was 127° (127-128° [8]).

e) 4,4'-Dinitro-2,2'-dimethoxybiphenyl. 100 g of electrolytic copper powder, activated by a solution of iodine in acetone [9], was added gradually over a period of two hours to 100 g of fused 2-methoxy-4-nitroiodobenzene heated to 230° in a flask of heat-resistant glass immersed in a metal bath. The powder was added at such a rate that the temperature of the fusion (thermometer in the fusion) was maintained constantly at the 230° level and the mixture was then kept at this temperature for a further 1.5 hours. Periodical stirring of the fusion with a copper spatula was necessary during the addition of the copper and subsequently. It should be mentioned that sometimes during the heating of the fusion with copper the temperature of the mixture began to rise very suddenly and spontaneously, charring of the organic matter and its partial dispersion in the form of dense yellow fumes occurring after 300°. To prevent this very undesirable phenomenon it was necessary to withdraw the flask from the bath as soon as the spontaneous rise in temperature was noticed and to cool it in a strong jet of cold tap water. When the temperature had fallen to the correct level, heating could be continued. On cooling, the hardened melt was crushed and the reaction product was extracted with small quantities of boiling toluene (about 2 liters in all). The combined extracts were treated with activated carbon, part of the reaction product being precipitated from the cooled solution but the major part separating out as a result of the evaporation of a considerable amount of the mother liquor. The total yield was 27 g (50%). After recrystallization from the toluene the m.p. was 247-248°. The crystals were greenish-yellow in color and the latter showed no appreciable change after repeated recrystallizations. It was noticed, however, that with strong heating above the temperature of the melting point the substance slowly sublimed in the form of long, almost white needles, melting at 248-249°; careful cleaning of this nature was not required for the synthetic operations described below because perfectly acceptable results were even ob-

tained from the uncrystallized product with an m.p. of 245-246°.

4,4'-Dinitro-2,2'-dimethoxybiphenyl is far less soluble in the usual organic solvents than the great majority of other known biphenyl derivatives of similar type.

Found %: N 9.12, 9.11. $C_{14}H_{12}O_6N_2$. Calculated %: N 9.21.

f) 4-Amino-4'-nitro-2,2'-dimethoxybiphenyl (VIII). 5 g of finely ground 4,4'-dinitro-2,2'-dimethoxybiphenyl was suspended in a mixture consisting of 500 ml of methyl alcohol in 35 ml of a 1 molar aqueous methanolic solution of sodium disulfide* The liquid was boiled with a reflux condenser for 2 hours, the solid matter gradually passing into solution. The solvent was then evaporated to a small volume and the residue was twice diluted with water. The precipitate formed was filtered, dried and dissolved in 60 ml of anhydrous nitrobenzene. If necessary this solution was filtered and a current of dry hydrogen chloride was passed into it until the hydrochloride of the amino derivative had been completely precipitated. The salt was filtered, carefully washed on the filter with ether and to purify the monoamine from an admixture of the more soluble diamine it was boiled with 200 ml of dilute hydrochloric acid (1 : 2), this operation being repeated again.

The free base was obtained by heating the hydrochloride with aqueous ammonia and it was then dissolved in methyl alcohol and treated with activated carbon. After the evaporation of part of the alcohol from the cooled solution crystals of the amine, melting at 161-162°, were precipitated. The yield was 3.2 g (71%). To further purify it the amine was recrystallized once more from methyl alcohol and then twice from benzene, as a result of which the temperature of the melting point was increased to 162-163°.

4-Amino-4'-nitro-2,2'-dimethoxybiphenyl was an orange-colored crystalline substance, reasonably soluble in the usual organic solvents. The reduction of the second nitro group in this compound with hydrazine hydrate in the presence of Raney nickel (see below) led to the formation of 2,2'-dimethoxybenzidine which was identical with a sample of the same amine synthesized by the benzidine rearrangement under conditions previously described [10].

Found %: NH_2 [11] 5.90, 5.81. $C_{14}H_{14}O_4N_2$. Calculated %: NH_2 5.84.

g) 4-Amino-2,2'-dimethoxybiphenyl (XI). 1) Deamidization of 4-amino-4'-nitro-2,2'-dimethoxybiphenyl. 2.6 g of 4-amino-4'-nitro-2,2'-dimethoxybiphenyl was dissolved in 35 ml of warm glacial acetic acid, 6 ml of concentrated hydrochloric acid was then added and the crystallized mixture was rapidly cooled to 0°. A cooled solution of 0.76 g of sodium nitrite in 7.6 ml of water was added gradually with efficient stirring to this mixture. The diazo solution obtained was filtered and added slowly to a mixture composed of 12 g of $NaH_2PO_2 \cdot H_2O$ and 12 ml of concentrated hydrochloric acid, cooled with ice. The reaction mass was well stirred and allowed to stand for a day at 15-18° in a loosely stoppered flask, after which the mixture was made alkaline with 20% NaOH and the oily product precipitated was extracted with ether. The ethereal solution was treated with activated carbon, the solvent was completely evaporated and the light-yellow oil remaining was kept in a vacuum desiccator, in which it acquired the consistency of a thick syrup; the yield was 1.6 g. In this form the deamidization product, which was impure 4-nitro-2,2'-dimethoxybiphenyl,** was subjected to a further operation — reduction.

2) Reduction of the deamidization product. 0.8 ml of 98% hydrazine hydrate was added to 1.6 g of impure 4-nitro-2,2'-dimethoxybiphenyl dissolved in 15 ml of hot methyl alcohol and this was followed by the gradual addition of Raney nickel, all the experimental procedures described in detail previously [4, 12] being observed. After the evolution of nitrogen had ceased a further 0.8 ml of hydrazine hydrate and more nickel catalyst were added. When the evolution of nitrogen had again ceased the solution was filtered without allowing it to cool, treated with activated carbon and the alcohol was completely evaporated. The residue, which after drying in a vacuum desiccator had the appearance of a dark oil, was dissolved in benzene and this solution was treated repeatedly with carbon after which the product was precipitated by passing a current of dry hydrogen chloride into the solution. The amine salt was filtered and washed with ether. The yield was 1 g (40%, on the basis of the initial 4-amino--4'-nitro-2,2'-dimethoxybiphenyl).

The free base was obtained by heating the hydrochloride with aqueous ammonia; it was first precipitated

* The solution was prepared in the following manner: 240 g of $Na_2S \cdot 9H_2O$ and 32 g of sulfur were heated moderately with 500 ml of water and 250 ml of methyl alcohol until complete solution took place; the cooled solution was then diluted to 1 liter.

** We did not undertake the experiment to isolate this compound in the pure crystalline state and we, therefore, cannot give any of its physicochemical constants.

in an oily state but after being washed with water and cooled, it crystallized. To purify them more carefully the grayish-white crystals of the amine were dissolved in benzene and the solution obtained was passed through a column filled with powdery aluminum oxide. The amine hydrochloride was again precipitated with hydrogen chloride and the free base was dissolved in a small quantity of boiling methyl alcohol. After treatment with activated carbon at a temperature near boiling this solution was gradually diluted with hot water until the appearance of turbidity. After cooling, the crystalline amine was precipitated and this was recrystallized from methyl alcohol several times until a constant melting point of 132-133° was obtained.

4-Amino-2,2'-dimethoxybiphenyl was a white crystalline substance, fairly readily soluble in the usual organic solvents.

Found %: NH_2 [11] 7.09, 7.00. $C_{14}H_{15}O_2N$. Calculated %: NH_2 6.99.

II. Synthesis of 4-Amino-4'-nitro-3,3'-dimethylbiphenyl and 4-Amino-3,3'-dimethylbiphenyl

A. Synthesis according to system 2. a) 4,4'-Dinitro-3,3'-dimethylbiphenyl (XIV) was obtained from o-tolidine according to a method described in literature [13] except for the difference that after the reaction was finished the product was not extracted with glycerin, as indicated in literature, but with boiling toluene from which the dinitro compound was subsequently also recrystallized.

b) 4-Amino-4'-nitro-3,3'-dimethylbiphenyl (XV). We developed a far more convenient method of synthesizing this amine than that described in literature [13]. 80 ml of a 1 molar solution of sodium disulfide in aqueous pyridine* was added to a solution of 11 g of 4,4'-dinitro-3,3'-dimethylbiphenyl in 40 ml of boiling pyridine (in a flask with a reflux condenser). The cooled solution was again brought to boiling which was continued for 30 minutes. The reaction product was precipitated by the addition of a large amount of hot water. After it had been filtered, washed with water and dried the precipitate was dissolved in toluene; the solution was treated with activated carbon and the amine was precipitated as the hydrochloride by passing dry hydrogen chloride. The free base was obtained by the decomposition of the hydrochloride by heating with aqueous ammonia. The yield was 6.7 g (68%). To purify it further the amine was treated twice again in the method described above and was first recrystallized twice from methyl alcohol, then 3 times from isopropyl alcohol and finally several times from toluene until a constant melting point of 143° was obtained (142-142.5° [13]).

c) 4-Nitro-3,3'-dimethylbiphenyl (XVII). The operations connected with the synthesis of this compound were similar to those described for the preparation of the analogous 2,2'-dimethoxy derivative (see section I, g): a diazo solution prepared from 3 g of 4-amino-4'-nitro-3,3'-dimethylbiphenyl, 25 ml of glacial acetic acid, 6 ml of concentrated hydrochloric acid and 1 g of sodium nitrite in 10 ml of water was treated with a mixture of 12.5 g of $NaH_2PO_2 \cdot H_2O$ and 12.5 ml of concentrated hydrochloric acid. After standing for a day the crystalline precipitate formed was filtered, washed with water and recrystallized from 90% (by volume) methyl alcohol with the addition of activated carbon. The m.p. was 70-71°. The yield was 1.5 g (60%).

4-Nitro-3,3'-dimethylbiphenyl was a crystalline product, faintly yellowish in color, readily soluble in alcohols, benzene and many other of the usual organic solvents; it was insoluble in water.

Found %: N 6.13, 5.91. $C_{14}H_{13}O_2N$. Calculated %: N 6.16.

d) 4-Amino-3,3'-dimethylbiphenyl (XVIII). As in the synthesis of the analogous 4-amino-2,2'-dimethoxybiphenyl (see, section I, g), the reduction of the 4-nitro-3,3'-dimethylbiphenyl was carried out by hydrazine hydrate in the presence of Raney nickel: a solution of 1.4 g of the nitro compound in 14 ml of hot methyl alcohol was treated once with 1.2 ml of 98% hydrazine hydrate with the gradual addition of nickel catalyst. Concentrated hydrochloric acid was added to the filtered and still-hot solution after the completion of the reaction until a definite acid reaction was obtained, a white precipitate of the amine hydrochloride being formed during this process. The salt was filtered and decomposed by heating slightly with aqueous ammonia. The amine which was precipitated in an oily state crystallized after washing with water and cooling. The dried product was dissolved in benzene (treatment with activated carbon) and was then precipitated as the hydrochloride by passing dry hydrogen chloride into the solution. The yield of amine after decomposition of the salt with ammonia was 1 g (82%), the m.p. was

* 240 g of $Na_2S \cdot 9H_2O$ and 32 g of sulfur were heated moderately with 600 ml of water and 100 ml of pyridine until complete solution took place, and the cooled solution was then diluted with water to 1 liter.

55-56°, and after recrystallization from methyl alcohol it was 57-58°.

Found %: NH_2 [11] 8.07, 8.10. $C_{14}H_{15}N$. Calculated %: NH_2 8.12.

B. Synthesis of 4-amino-3,3'-dimethylbiphenyl according to system 3. 64 g of o-tolidine was dissolved with heating in 3 liters of water in 120 ml of concentrated hydrochloric acid. The mixture which was cooled rapidly to +5-8° was diazotized with a solution of 21 g of sodium nitrite in 120 ml of water and the diazo solution obtained was allowed to stand at 12-15°. After 3 days the solution was filtered and poured into 360 ml of a cooled solution of hypophosphorous acid. The mixture was stirred well and again allowed to stand for 2 days at room temperature. The dark, flocculent, sticky precipitate formed was separated as far as possible from the liquid by decantation and in that way was washed with dilute aqueous ammonia and then with water. The reaction product was extracted with boiling benzene; this solution was treated several times with activated carbon, dried with anhydrous sodium sulfate and was finally passed through a column filled with aluminum oxide. The yield of the amine hydrochloride, isolated from the benzene solution by means of hydrogen chloride, was 16 g (23%). To further purify it the salt was again recrystallized three times from a mixture of equal volumes of water, concentrated hydrochloric and glacial acetic acids and the same number of times from aqueous hydrochloric acid (1 : 1). The free base obtained by the decomposition of the hydrochloride by ammonia was again recrystallized several times from methyl alcohol; the m.p. was 57-58°. A mixed melt of this sample with the product obtained according to system 2 showed no depression of the melting point.

4-Amino-3,3'-dimethylbiphenyl was a white crystalline substance, almost insoluble in water but readily soluble in the usual organic solvents. Like its methoxy analog described above, this amine forms completely stable and easily crystallizable salts with strong mineral acids.

SUMMARY

1. 4,4'-Dinitro-2,2'-dimethoxybiphenyl; 4-amino-4'-nitro-2,2'-dimethoxybiphenyl; 4-amino-2,2'-dimethoxybiphenyl; 4-nitro-3,3'-dimethylbiphenyl and 4-amino-3,3'-dimethylbiphenyl, not previously described in literature, were synthesized.

2. Existing methods were improved and new methods developed for preparing a number of intermediate products, necessary for the synthesis of the above-mentioned biphenyl derivatives.

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CATALYTIC CONDENSATION OF ACETYLENE WITH AROMATIC AMINES

XXX.* CATALYTIC SYNTHESIS OF m-NITRO, AMINO, AND SULFONAMIDO DERIVATIVES OF 2-PHENYLQUINOLINE AND 2-PHENYL-5,6-BENZOQUINOLINE

N. S. Kozlov and O. K. Kozminykh

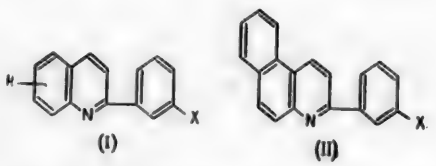
Nitro and amino derivatives of 2-phenylquinoline and 2-phenyl-5,6-benzoquinoline have almost not been studied at all. Several such derivatives [2-4] have been prepared by the Doebner-Miller method [1]. In the present work we have continued the investigation of the catalytic co-condensation of acetylene with aromatic amines and aromatic aldehydes [5-7] and have succeeded in developing a new use of this reaction for the synthesis of nitro derivatives of 2-phenylquinoline, and from the nitro derivatives have accomplished the preparation of new amino and sulfamido derivatives of 2-phenylquinoline. The sulfamides of the quinoline series have practically not been studied [8, 9], although there are data [10, 11] concerning their marked antibacterial action.

For the synthesis of the nitro derivatives we used in the reaction the aromatic amines aniline, m- and p-toluidine, p-anisidine, p-phenetidine, and β-naphthylamine; of the aromatic aldehydes we used m-nitrobenzaldehyde. A series of nitro derivatives of 2-phenylquinoline and 2-phenyl-5,6-benzoquinoline was synthesized (Table 1, compds. I-VI). Of the compounds given, I [2, 12, 13], IV [3, 14], and VI [4] had been described in the literature, and II, III, and V were prepared by us for the first time. A difference in the melting points of the compound VI prepared by us and that described by N. Gallo [4] was noted. N. Gallo did not confirm the composition of the compound by elementary analysis, but only analyzed the platinate.

The nitro compounds prepared by us were converted to the amines by the usual reduction methods (Table 1, compds. VII-IX).

Starting with the amines that were isolated, we prepared by a known method [15] a series of sulfonamido derivatives of 2-phenylquinoline and 2-phenyl-5,6-benzoquinoline that had not been described in the literature (Table 2, compds. X-XXX).

Thus, we synthesized the compounds with the general formulas I and II:



(I) (II)

R=CH_3, OCH_3, OC_2H_5; X = NO_2, NH_2, $NHSO_2C_6H_4NHCOCH_3$-p, $NHSO_2C_6H_4NH_2$-p, $NHSO_2C_6H_5$, $NHSO_2C_6H_4NHCOCH_3$-m, $NHSO_2C_6H_4NH_2$-m, $NHSO_2C_6H_4OCH_3$-p, $NHSO_2$–

EXPERIMENTAL

The preparation of m-nitro derivatives of 2-phenylquinoline can be carried out in two ways. By the first

* For previous communication see Proc. Acad. Sci. USSR, 14, 785 (1957) (See C. B. Translation).

TABLE 1

Compound No.	Compound	Melting point	Analysis of compounds (in %)						Melting point of picrate	Analysis of platinate for Pt content (%)	
			N		H		C				
			calculated	found	calculated	found	calculated	found		calculated	found
I	2-(3'-Nitrophenyl)quinoline	122—123° (123—124 [12])	—	—	—	—	—	—	179—180° (181 [13])	—	—
II	6-Methyl-2-(3'-nitrophenyl)quinoline	142—142.5	10.60	10.52. 10.45	4.57	4.60. 4.52	72.71	72.68. 72.59	190—190.5	20.80	20.50
III	7-Methyl-2-(3'-nitrophenyl)quinoline	158	10.60	10.66. 10.74	4.57	4.43. 4.51	72.71	72.52. 72.77	185—186	20.80	20.53
IV	6-Methoxy-2-(3'-nitrophenyl)quinoline	135.5—136 (130 [14])	9.99	9.77. 9.94	4.31	4.27. 4.22	68.56	68.51. 68.63	196—197	20.11	19.82
V	6-Ethoxy-2-(3'-nitrophenyl)quinoline	142.5—143	9.51	9.37. 9.38	4.79	4.91. 4.96	69.37	69.29. 69.57	235—236	19.65	19.63
VI	2-(3'-Nitrophenyl)-5,6-benzoquinoline	182—183 (168 [4])	9.32	9.29. 9.50	4.02	4.18. 4.18	75.98	75.87. 76.13	240 (decomp)	19.31	19.46
VII	6-Methoxy-2-(3'-aminophenyl)-quinoline	127—128 (127 [16])	11.19	11.45. 11.42	—	—	—	—	233—235 (decomp.)	21.44	21.28
VIII	6-Ethoxy-2-(3'-aminophenyl)-quinoline	159—160	10.59	10.93. 10.79	6.10	6.12. 6.13	77.24	77.38. 77.06	202(decomp.)	20.79	20.50
IX	2-(3'-Aminophenyl)-5,6-benzoquinoline	218—219	10.36	10.37. 10.20	5.22	5.01. 5.03	84.41	84.58. 84.43	245—246 (decomp.)	20.53	20.46

TABLE 2

Compound No.	Compound	Melting point	Analysis for nitrogen (in %)	
			calculated	found
X	6-Methoxy-2-(3'-p-acetoamidobenzenesulfonamidophenyl)quinoline	217—218°	9.39	9.11, 8.97
XI	6-Methoxy-2(3'-p-aminobenzenesulfonamidophenyl)quinoline	195—196	10.36	10.12, 10.10
XII	6-Methoxy-2-(3'-benzenesulfonamidophenyl)quinoline	191—192	7.17	6.73, 6.95
XIII	6-Ethoxy-2-(3'-p-acetamidobenzenesulfonamidophenyl)quinoline	219	9.10	9.01, 9.17
XIV	6-Ethoxy-2-(3'-p-aminobenzenesulfonamidophenyl)quinoline	213—214	10.17	9.86, 10.01
XV	6-Ethoxy-2-(3'-benzenesulfonamidophenyl)quinoline	208—209	6.92	6.66, 6.70
XVI	2-(3'-p-Acetamidobenzenesulfonamidophenyl)-5,6-benzoquinoline	233—234 (decomp.)	8.98	9.24, 9.02
XVII	2-(3'-p-Aminobenzenesulfonamidophenyl)-5,6-benzoquinoline	224 (decomp.)	9.87	10.10, 10.07
XVIII	2-(3'-Benzenesulfonamidophenyl)-5,6-benzoquinoline	201—202	6.82	6.56, 6.69
XIX	6-Methoxy-2-(3'-m-acetamidobenzenesulfonamidophenyl)quinoline	214—215	9.39	9.52, 9.62
XX	6-Methoxy-2-(3'-m-aminobenzenesulfonamidophenyl)quinoline	227—228 (decomp.)	10.36	10.27, 10.32
XXI	6-Ethoxy-2-(3'-m-acetamidobenzenesulfonamidophenyl)quinoline	199—200.5	9.10	8.93, 9.09
XXII	6-Ethoxy-2-(3'-m-aminobenzenesulfonamidophenyl)quinoline	203—204	10.17	10.25
XXIII	2-(3'-m-Acetamidobenzenesulfonamidophenyl)-5,6-benzoquinoline	237—238	8.98	8.81, 8.79
XXIV	2-(3'-m-Aminobenzenesulfonamidophenyl)-5,6-benzoquinoline	199—200	9.87	9.57, 9.64
XXV	6-Methoxy-2-(3'-p-methoxybenzenesulfonamidophenyl)quinoline	137—138	6.66	6.44, 6.51
XXVI	6-Ethoxy-2-(3'-p-methoxybenzenesulfonamidophenyl)quinoline	183—184	6.44	6.41, 6.52
XXVII	2-(3'-p-Methoxybenzenesulfonamidophenyl)-5,6-benzoquinoline	170—171	6.36	6.05, 6.24
XXVIII	2-(3'-β-Pyridylsulfonamidophenyl)-5,6-benzoquinoline	174—175	10.21	10.11, 10.35
XXIX	6-Methoxy-2-(3'-β-pyridylsulfonamidophenyl quinoline	190—190.5	10.73	10.85, 10.75
XXX	6-Methoxy-2-(3'-β-pyridylsulfonamidophenyl) phenyl)quinoline	209—210	10.36	10.14, 10.23

method, a mixture of 2 g-moles of aromatic amine and 1 g-mole of aromatic aldehyde is taken, dissolved in an appropriate solvent, mixed with catalyst, and the mixture is saturated with acetylene [5, 6]. We used a second method, by which the Schiff base was first separated as a crystalline product from m-nitrobenzaldehyde and aromatic amine dissolved in alcohol by heating; the Schiff base was again dissolved in alcohol or toluene, mixed with an equimolecular amount of aniline, and the reaction mixture was saturated with acetylene in the presence of a catalyst – mercuric chloride – over a period of 15-20 hours while heating on a water bath at 70-80°. During the first hours of the experiment the acetylene was actively absorbed by the reaction mixture and a precipitate formed, which at the end of the saturation period occupied not less than $^1/_3$ of the volume of the reaction mixture and was a dark, tarry mass. Then an excess of alkali was added to the mixture and the volatile materials (aniline and solvent) were steam-distilled off and the tar solidified to a firm, brittle mass colored different shades of orange. The tar thus purified was dissolved in a mixture of alcohol and concentrated hydrochloric acid in the ratio 2 : 1 and was heated for 1 hour on a water bath. Under these conditions the intermediate reaction products were cyclized to the quinoline bases and the hydrochloride of the product that formed usually precipitated after the mixture was cooled as an amorphous or crystalline mass, which was separated, purified by recrystallization, and after treatment with ammonia was converted to the free base. If the hydrochloride of the product did not precipitate, then the solution was treated with ammonia and the precipitate of base was separated and purified in the usual way.

The catalyst in the reaction process underwent a transformation, the details of which have not been clarified: in the first phase the mercuric chloride was converted into mercury acetylide, which further formed a complex with the reaction products that settled as a heavy precipitate; the latter was broken down by the alkali, and after the steam-distillation droplets of metallic mercury remained in the tar.

When toluene was used as the solvent, we did not resort to steam-distillation but immediately treated the reaction mass with a 10% solution of HCl in alcohol and after the mixture was cooled we poured off the toluene layer, in which the greater part of the impurity was contained. The yield of pure product was not less than 40%, and in isolated cases was 50-60%.

The nitro compounds were converted to the amines by the known method. The sulfonamido derivatives were obtained by the method described in the typical experiments presented below, by condensation in pyridine medium of the amines prepared by us with different sulfonic acid chlorides – benzenesulfonyl chloride, m- and p-acetamidobenzenesulfonyl chlorides, p-methoxybenzenesulfonyl chloride, and β-pyridinesulfonyl chloride.

As an example a description is given of the experiments on the synthesis of the nitro-, amino-, and sulfonamido derivatives of 2-phenylquinoline, which are typical of the synthesis of the other similar compounds.

6-Ethoxy-2-(3'-nitrophenyl)quinoline. From 30 g (0.1985 g-mole) of m-nitrobenzaldehyde and 27.2 g (0.1983 g-mole) of freshly distilled p-phenetidine we prepared the Schiff base – a yellow, crystalline product with m.p. 100°. To a solution of the Schiff base in toluene (100 ml) was added 20 g (0.2 g-mole) of freshly distilled aniline and 6 g of mercuric chloride, and the mixture was saturated with acetylene for 18 hours while being heated on the water bath to 80°. At the end of the reaction 40 ml of concentrated hydrochloric acid and 80 ml of alcohol were added to the reaction mass and the mixture was heated for 1 hour on the water bath. After this, the toluene layer was decanted and the alcohol solution, previously separated from the precipitate of catalyst, was cooled. The hydrochloride that had separated out in the precipitate was isolated, washed with alcohol and acetone, then dissolved in alcohol and treated with aqueous ammonia. The base that was separated was crystallized from acetone. 28.5 g (50%) of a yellow, crystalline product was obtained.

6-Ethoxy-2-(3'-aminophenyl)quinoline. A mixture of 25 g of 6-ethoxy-2-(3'-nitrophenyl)quinoline, 80 ml of concentrated hydrochloric acid, and 160 ml of alcohol was heated on a water bath to 80°, and into it was introduced 25 g of granulated tin. After the mixture had been heated for 8 hours, a concentrated solution of sodium hydroxide was added to the cooled mass until the reaction was alkaline, the precipitate was separated and dried and extracted with acetone in a Soxhlet apparatus. The compound separated from the acetone solution as yellow needles. Yield 20 g (80%). After 2 recrystallizations from pyridine and acetone the material was obtained with m.p. 159-160° as colorless needles.

6-Ethoxy-2-(3'-p-acetamidobenzenesulfonamidophenyl)quinoline. To 2 g (0.00752 g-mole) of 6-ethoxy-2-(3'-aminophenyl)quinoline dissolved in 3 ml of dry pyridine was added a solution of 1.77 g (0.00753 g-mole) of p-acetamidobenzenesulfonyl chloride in 4 ml of dry pyridine, and the solution was heated for 2 hours on a water bath to 70-80°. After the solution was cooled, 2 ml of water was added and a yellow oil separated out, which quickly crystallized. Crystallization from acetone yielded coarse, white prisms with m.p. 219°.

6-Ethoxy-2-(3'-p-aminobenzenesulfonamidophenyl)quinoline. 1.3 g of 6-ethoxy-2-(3'-p-acetamidobenzenesulfonamidophenyl)quinoline was heated for 4 hours on a water bath in 50 ml of 5% sulfuric acid solution. At the end of the heating period the material was filtered off, washed with ammonia, and crystallized from acetone. 1 g of a white, finely crystalline powder was obtained with m.p. 213-214°.

6-Ethoxy-2-(3'-benzenesulfonamidophenyl)quinoline. To a solution of 1.5 g (0.00567 g-mole) of 6-ethoxy-2-(3'-aminophenyl)quinoline in 4 ml of dry pyridine was added a solution of 1 g (0.00568 g-mole) of freshly distilled benzenesulfonyl chloride in 2 ml of dry pyridine, and the mixture was heated for 2 hours on a water bath to 70-80°. After cooling, the material partially crystallized out, and it was completely precipitated by adding 3 ml of water. Crystallization from acetone yielded 1.8 g of white, fine crystals with m.p. 208-209°.

SUMMARY

A series of nitro, amino, and sulfonamido derivatives of 2-phenylquinoline and 2-phenyl-5,6-benzoquinoline has been synthesized, of which 26 compounds had not been described in the literature.

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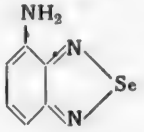
SOME NEW DERIVATIVES OF PIASELENOLE AND THEIR ABSORPTION SPECTRA*

L. S. Efros and Z. V. Todres-Selektor

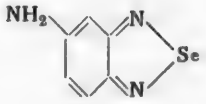
In a publication by one of us with R. M. Levit [1] there were presented the results of the measurement of the absorption spectra of a number of derivatives of piazothiole, which to a noted extent confirmed the quinoid structure of the benzene ring of this compound.

The present work was devoted to similar investigations of derivatives of piaselenole and comparison of their absorption spectra with the spectra of the piazothiole derivatives.

The starting materials for the synthetic portion of the work were the isomeric 4-aminopiaselenole (I) and 5-aminopiaselenole (II), the synthesis of which was described in previous communication [2].

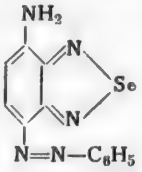


(I)

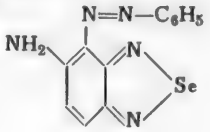


(II)

By the action of acetic anhydride under the usual conditions these amines form the corresponding acetyl derivatives. The amines (I) and (II) enter with great ease into a coupling reaction with diazotized aniline, yielding the azo dyes (III) and (IV), which we were able to purify and analyze.



(III)



(IV)

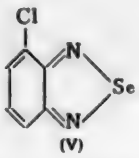
The p-aminoazo dye (III) dissolved readily in mineral acids, yielding salts more deeply colored than the base. The ortho-isomer (IV), like most o-aminoazo compounds, did not give salts with acids.

The lowered basicity of the isomeric amines (III) and (IV) [2] and the easy course of the azo coupling reaction are evidence of a considerable shift of the unshared electron pair of the nitrogen atoms of their amino groups to the benzene ring, which is impoverished of electrons because of the strong electronophilic action of the hetero ring [3].

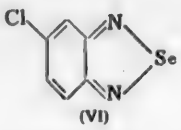
Because of the ease with which these amines enter into the azo coupling reaction, their diazotization must be carried out in concentrated hydrochloric acid.

The diazo compounds from the aminopiaselenoles pass over in good yield by the Sandmeyer reaction to the corresponding 4- and 5-chloropiaselenoles (V) and (VI).

* We could not refer to the work of E. Sawicki and Carr [6] since it was published after our article was submitted to the printer.



(V)



(VI)

Thus, the isomeric aminopiaselenoles differ very little in their chemical properties from the previously studied compounds containing sulfur.

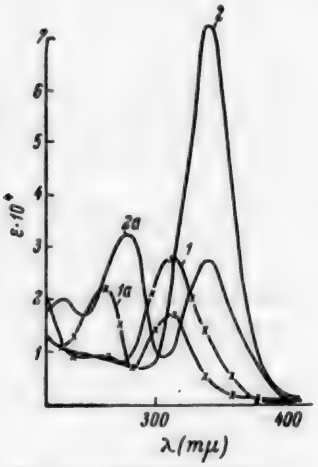


Fig. 1. Absorption spectra. 1) 4-Nitropiaselenole, 2) 4-nitropiazothiole, 1a) 5-nitropiaselenole, 2a) 5-nitropiazothiole.

The results of the measurements of the absorption spectra of the piaselenole derivatives and their comparison with the spectra of the analogous piazothiole derivatives* are given in Figs. 1-5 (see also Fig. 1 in the previous communication [2]).

For piazothiole there are two very intense, characteristic, narrow absorption bands in the ultraviolet region at 220 and 305 mμ (corresponding $\epsilon = 10^4$ 2.24 and 2.28), the presence of which could be traced in all of the derivatives studied by us.

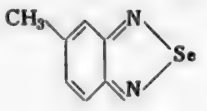
In the absorption spectra of piaselenole and its derivatives similar bands were detected, somewhat shifted to the long-wave region. For piaselenole itself they were found at 230-330 mμ, while the intensity of the first band was less, but that of the second was considerably greater, than in the spectrum of piazothiole ($\epsilon = 10^4$ 0.86 and 3.34).

Introduction of the amino group into the 4- or 5-position of the piazothiole and piaselenole molecules moved the first absorption band of these compounds by 15-20 mμ in the long-wave direction and made them considerably more intense. The second absorption band remained almost without change, but in the visible region three absorption maxima appeared, which were at 400-420 mμ for the aminopiazothioles and at 430-460 mμ for the piaselenole derivatives, and the orange color of the latter was weakened. Acetylation of the amino groups had little effect on the position of the first two absorption bands, but the third shifted toward the shorter waves.

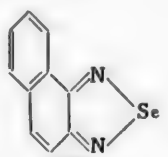
Introduction of the nitro group weakened and shifted the first two bands to the short-wave region and caused the appearance of an intense third band at the boundary of the visible region at 315 mμ for piazothiole and at 340 mμ for piaselenole derivatives.

Introduction of a chlorine atom did not cause a perceptible change in the position of the maxima in the absorption curves.

In the absorption spectra of 5-methylpiaselenole (VII) and 4,5-benzopiaselenole (VIII) (Fig. 5) a series of closely positioned maxima was observed (fine structure). It is interesting to note that for the latter compound these maxima correspond to almost the same wavelengths as those for unsubstituted naphthalene [4].



(VII)



(VIII)

* The absorption spectra of the derivatives of piaselenole and piazothiole were determined with an SF-4 spectrophotometer. For all the compounds the measurements were made in alcohol solutions, within the limits of the wavelengths 215-650 mμ, every 5-10 mμ.

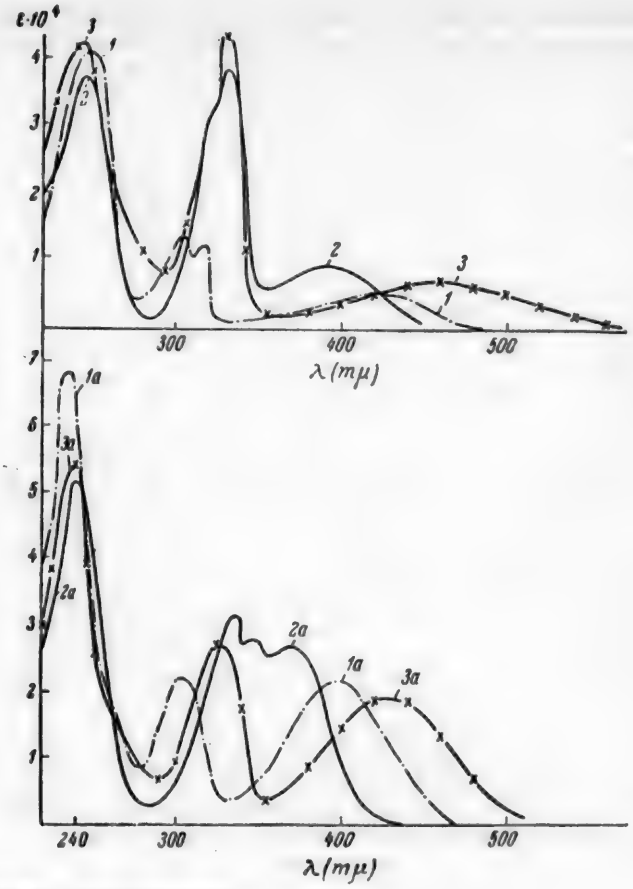


Fig. 2. Absorption spectra.
1) 4-Aminopiazothiole, 2) 4-acetamidopiaselenole, 3) 4-aminopiaselenole, 1a) 5-aminopiazothiole, 2a) 5-acetamidopiaselenole, 3a) 5-aminopiaselenole.

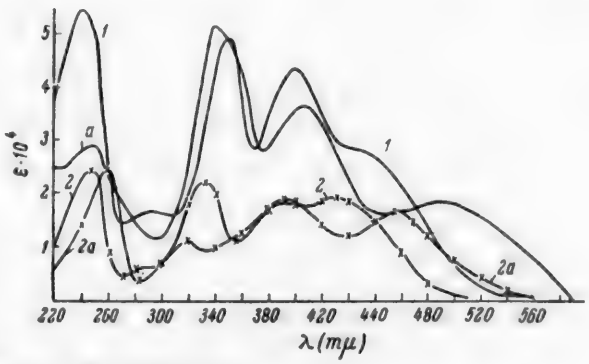


Fig. 3. Absorption spectra.
1a) 7-Phenylazo-4-aminopiaselenole, 2a) 7-phenylazo-4-aminopiazothiole, 1) 4-phenylazo-5-aminopiaselenole, 2) 4-phenylazo-5-aminopiaselenole.*

* As in original. Curve 2) apparently refers to 4-phenylazo-5-aminopiazothiole — Publisher's note.

The spectra of the aminoazo dyes (III) and (IV) were very close to the spectra of the corresponding dyes of the piazothiole series, but the positions of the maxima for (III) and (IV) were somewhat shifted in the long-wave direction.

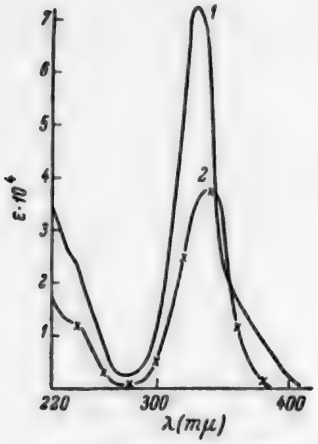


Fig. 4. Absorption spectra.
1) 4-Chloropiaselenole,
2) 5-chloropiaselenole.

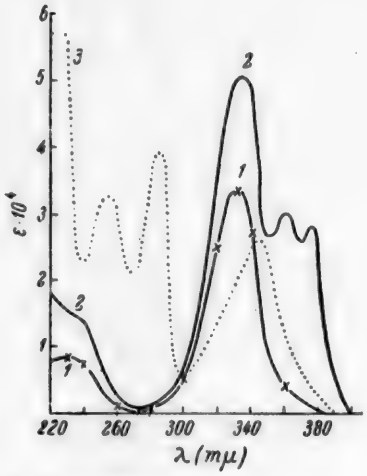


Fig. 5. Absorption spectra.
1) Piaselenole, 2) 5-methylpiaselenole,
3) benzo-(4,5)-piaselenole (1,2-naphthoseledíazole).

Thus, while there was a considerable similarity in the course of the absorption curves of the derivatives of piazothiole and piaselenole, the piaselenoles absorbed in the longer wave region and were more deeply colored than the former. It is clear that the lesser affinity of the selenium atom than that of sulfur for electrons provides a greater mobility of the electrons in the piaselenole molecule. Thus, in going from the pyridyl aryl sulfides to the pyridyl aryl selenides there is also a corresponding bathochromic shift [5].

The differences that have been noted between the piaselenole derivatives and the corresponding piazothiole derivatives confirm, it seems to us, the previously proposed assumption [2] concerning the more quinoid character of the structure of the piaselenole derivatives.

EXPERIMENTAL

4-Acetamidopiaselenole. In a 50-ml flask fitted with a reflux condenser were placed 1 g of 4-aminopiaselenole and 3.7 g of acetic anhydride. The flask was heated for a half-hour on a boiling water bath. Then the contents of the flask were transferred to a beaker with a small amount of water. The mixture was heated to boiling and neutralized with ammonia. Yellow plates of the acetyl derivative precipitated. Upon cooling of the mass, they were filtered off and washed with a small amount of water. Yield 1.15 g (95%). The compound was crystallized from water with activated carbon. Dark yellow, long needles separated, which melted at 175-176° (decomp.).

The product was soluble in organic solvents, slightly soluble in cold water and very soluble in hot water.

Found %: N 17.49, 17.46. $C_9H_7ON_3Se$. Calculated %: N 17.50.

5-Acetamidopiaselenole. Under the conditions described above, 0.5 g of 5-aminopiaselenole was acetylated with 1.4 g of acetic anhydride. 0.55 g (91%) of a light brown product was obtained. The compound was crystallized from alcohol with activated carbon. Light yellow plates were obtained with m.p. 257.5-258.5°. Upon crystallization from 98% acetic acid, fine, light yellow plates separated with m.p. 259°. The compound was poorly soluble in ethyl alcohol, acetone, and water; it was completely insoluble in benzene and ether; very soluble in methyl alcohol and acetic acid.

Found %: N 17.53, 17.47. $C_9H_7ON_3Se$. Calculated %: N 17.50.

7-Phenylazo-4-aminopiaselenole. 1 g of 4-aminopiaselenole was dissolved in 100 ml of 10% hydrochloric acid. The solution was added gradually, with stirring, at 0-2° to a solution of diazobenzene prepared from 0.66 g of aniline hydrochloride. Almost immediately the liquid acquired an intense cherry red color. Sodium acetate was added to the mixture until there was no acid reaction to congo. After 1-2 hours the thick, dark red mass was separated and washed with water. The azo dye remained on the filter as a dark tar. The material was dried at 60-70°. 1.4 g (92% calculated on the basis of the azo dye) of a dark red powder was obtained, which melted at 143-148° (decomp.). The precipitate obtained was treated with carbon in boiling ethyl alcohol and, by adding water to the alcohol solution, the pure dye was separated. The dry dye looked like a dark powder; under the microscope it had the form of regular, tetrahedral prisms. M.p. 161-161.8° (decomp.).

The dye was readily soluble in alcohol, ether, and acetone, less so in benzene; it was insoluble in water; it dissolved in hydrochloric acid with a deepening of the color. From the hydrochloric acid solution it was possible to precipitate with ammonia the cherry red base of the azo dye.

Found %: C 47.41, 47.09; H 3.41, 2.62; N 23.14, 23.05. $C_{12}H_9N_5Se$. Calculated %: C 47.68; H 2.98; N 23.18.

4-Phenylazoaminopiaselenole. The coupling reaction was carried out just as described above, but the red-orange precipitate of the azo dye separated as soon as the first drops of amine solution were added to the solution of diazobenzene in the hydrochloric acid medium. If, after the two solutions had been poured together, sodium acetate was added, then the orange precipitate that had separated previously darkened and a lower yield was obtained. Therefore it was more convenient to neutralize the amine solution with excess sodium acetate and to partially neutralize the diazobenzene solution before coupling. When such solutions were poured together, the dye separated as reddish-orange plates. Yield 80% (from 1 g of amine 1.22 g of azo dye was obtained).

The product was insoluble in water and in hydrochloric acid; it was readily soluble in organic solvents, with an orange coloration. The dye was purified by crystallization from alcohol with activated carbon. Fine orange plates were obtained. M.p. 199-201°.

Found %: N 23.26, 23.27. $C_{12}H_9N_5Se$. Calculated %: N 23.18.

4-Chloropiaselenole. 1.3 g of 4-aminopiaselenole was dissolved in 80 ml of 25% hydrochloric acid. A solution of 1 g of sodium nitrite was added gradually, with stirring, at 0° until there was a positive reaction with starch-iodide paper. A light red, clear solution of diazopiaselenole was obtained. The excess nitrous acid was removed by adding urea. Then the solution was slowly added, with stirring, to a solution of cuprous chloride, cooled to 0°, which was prepared by the reduction of 6 g of copper sulfate with 30 ml of 38% sodium bisulfite solution. A dark precipitate separated. The mixture was allowed to stand for 1.5-2 hours, and then was heated in a flask with a reflux condenser on a water bath at 60-80° until the evolution of nitrogen bubbles ceased. After this the mixture was subjected to steam distillation. With the first portions of the distillate 0.5 g (37%) of a colorless substance was distilled off with m.p. 160-162° (after drying at 90-100°).

After recrystallization from small amounts of alcohol, white lamellae were obtained with m.p. 161-162° (with sublimation). The compound was readily soluble in alcohol, ether, and benzene.

Found %: C 33.00, 33.00; H 2.08, 1.90; N 12.83, 12.82. $C_6H_3ClN_2Se$. Calculated %: C 33.10; H 1.38; N 12.87.

5-Chloropiaselenole. 5-Chloropiaselenole was prepared by the Sandmeyer reaction under the conditions for the preparation of 4-chloropiaselenole. The diazo compound was prepared from 5-aminopiaselenole by treating the amine solution in concentrated hydrochloric acid with nitrite. From 1.3 g of aminopiaselenole 0.45 g (30%) of 5-chloropiaselenole was obtained. M.p. 117-118°. This product had been described by us previously [2].

SUMMARY

1. The isomeric 4- and 5-aminopiaselenoles, like the aminopiazothioles, have the properties of aromatic amines; they are easily acetylated, diazotized, and coupled with diazo compounds.

2. An investigation of the absorption spectra of piaselenole and some of its derivatives confirmed the assumption suggested earlier that piaselenole is closer in its character to o-quinonediimine than is piazothiole.

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Lensovet Leningrad Technological Institute

*Original Russian pagination. See C. B. Translation.

SYNTHESIS OF BICYCLIC SYSTEMS, STARTING FROM 2,6-LUTIDINE

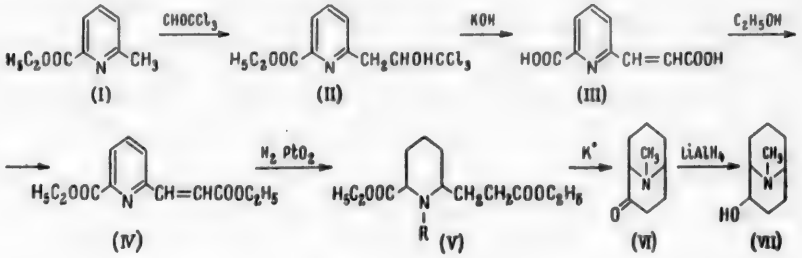
I. SYNTHESIS OF 9-METHYL-2-HYDROXY-9-AZABICYCLO (3,3,1) NONANE

E. S. Nikitskaya and M. V. Rubtsov

Study of the azabicyclo compounds of the octane series (quinuclidine, tropane) has shown that they are of considerable interest as starting materials for the synthesis of medicinal substances. In particular, in the investigation of tropine derivatives compounds were discovered that had curarelike, ganglion-blocking, spasmolytic, mydriatic, and other properties [1].

It seemed to us to be of interest to study bicyclic systems close to the tropane series. In this connection we synthesized 9-methyl-2-hydroxy-9-azabicyclo(3,3,1)nonane, starting with the ethyl ester of 6-methylpicolinic acid, which was prepared in turn from 2,6-lutidine.

The synthesis was accomplished by the following scheme



(Va) R = H (Vb) R = $COCH_3$ (Vc) R = CH_3

The ethyl ester of 6-methylpicolinic acid (I) was condensed with chloral in the presence of piperidine acetate. The condensation product (II) was saponified with alcoholic potassium hydroxide and the 2-carboxy-6-(β-carboxyvinyl)pyridine (III) produced in this way was converted to 2-carboethoxy-6-(β-carboethoxyvinyl)pyridine (IV). By hydrogenation of (IV) in the presence of platinum black, 2-carboethoxy-6-(β-carboethoxyethyl)piperidine (Va) was obtained. This compound, like its acetyl derivative (Vb), was converted by cyclization by the method of Dieckmann to a tarry mass, from which it was not possible to isolate the individual substance.

Use of the N-methyl derivative (Vc) for the cyclization permitted us to obtain, in 11% yield, 9-methyl-2-keto-9-azabicyclo(3,3,1)nonane (VI) which is an isomer of pseudopelletierine. By reduction of (VI) with lithium aluminum hydride we obtained 9-methyl-2-hydroxy-9-azabicyclo(3,3,1)nonane.

EXPERIMENTAL

2-Carboethoxy-6-(β-hydroxy-γ,γ,γ-trichloropropyl)pyridine (II). A mixture of 2.4 g of the ethyl ester of 6-methylpicolinic acid, 2.16 g of freshly distilled chloral, 10 ml of anhydrous xylene, 7 drops of piperidine, and 5 drops of glacial acetic acid was heated for 20 hours at 150° (in a bath). At the end of the reaction the dark brown mass was extracted with 10% hydrochloric acid. The acid extract was treated with carbon, filtered, and the 2-carboethoxy-6-(β-hydroxy-γ,γ,γ-trichloropropyl)pyridine was separated from the filtrate as a white, crystalline precipitate by the addition of 15% sodium carbonate solution. Yield 2.25 g (46.4%). The compound contained

1 mole of water of crystallization, which it lost upon drying in a vacuum desiccator over sulfuric acid, being converted in this process to a brown liquid that decomposed when distilled in vacuo. The hydrate after crystallization from 50% aqueous alcohol melted at 79-81°. It was soluble in the usual organic solvents, insoluble in water.

Found %: C 39.70; H 4.30; N 4.05; Cl 31.97. $C_{11}H_{12}O_3NCl_3 \cdot H_2O$. Calculated %: C 39.96; H 4.26; N 4.26; Cl 32.17.

2-Carboethoxy-6-(β-carboethoxyvinyl)pyridine (IV). Solutions of 10 g of 2-carboethoxy-6-(β-hydroxy-γ,γ,γ-trichloropropyl)pyridine in 70 ml of anhydrous ethyl alcohol and 14.3 g of potassium hydroxide in 70 ml of anhydrous ethyl alcohol were mixed. The mixture was heated for 2 hours at 60° (in a bath) and for 1 hour at the boiling point of the reaction mass. Then a current of carbon dioxide gas was passed through the reaction mixture at 60° until the alkaline reaction to phenolphthalein disappeared. The precipitate was filtered off, transferred to a flask, and boiled twice with 50 ml of anhydrous ethyl alcohol, with subsequent filtration. The alcoholic filtrates were combined together and evaporated to dryness in vacuo. To the residue was added 65 ml of 6% alcoholic solution of hydrogen chloride and the mixture was heated on a boiling water bath for 3 hours. The precipitate of potassium chloride that separated was filtered off, the solution was evaporated, 65 ml of 6% alcoholic solution of hydrogen chloride was again added to the residue, and the mixture was boiled for 3 hours. After the solution was evaporated in vacuo, the residue was treated with an excess of 50% potassium carbonate solution and extracted with ether. The ether extract was dried with anhydrous sodium sulfate and the ether was distilled off. The residue was distilled in vacuo. 2.73 g (36.4%) was obtained of a light yellow, oily liquid with b.p. 166-168° (1 mm). The material was soluble in the usual organic solvents, insoluble in water, and gave a reaction for a double bond.

Found %: N 5.47, 5.54. $C_{13}H_{15}O_4N$. Calculated %: N 5.62.

2-Carboethoxy-6-(β-carboethoxyethyl)piperidine (Va). 3.45 g of 2-carboethoxy-6-(β-carboethoxyvinyl)-pyridine was dissolved in 35 ml of anhydrous ethyl alcohol, 20% alcohol solution of hydrogen chloride was added until there was an acid reaction to congo, and the reaction mixture was hydrogenated in the presence of 0.2 g of platinum dioxide under the pressure of a 30-40-cm column of water. Absorption was completed in 8 hours. The catalyst was filtered off, the solution was evaporated in vacuo, and the residue was treated with an excess of 50% potassium carbonate solution and extracted with ether. The ether extract was dried with anhydrous sodium sulfate, the ether was distilled off, and the residue was distilled in vacuo. B.p. 152° (0.35 mm). A colorless, oily material was obtained that was readily soluble in the usual organic solvents and in water. Yield 3.1 g (87%).

B.p. 152° (0.35 mm), n_D^{22} 1.4599.

Found %: C 60.46; H 8.97. $C_{13}H_{23}O_4N$. Calculated %: C 60.67; H 9.00.

The hydrochloride was a white, crystalline compound with m.p. 110°.

2-Carboethoxy-6-(β-carboethoxyethyl)-N-acetylpiperidine (Vb). 4.7 g of 2-carboethoxy-6-(β-carboethoxyethyl)piperidine was heated for 2 hours on a boiling water bath with 50 ml of acetic anhydride. After the excess acetic anhydride was distilled off, the residue was distilled in vacuo. 3.9 g (73%) was obtained of an immobile liquid with a straw-yellow color. B.p. 180-182° (0.75 mm).

Found %: N 4.51; 4.48. $C_{15}H_{25}O_5N$. Calculated %: N 4.63.

2-Carboethoxy-6-(β-carboethoxyethyl)-N-methylpiperidine (Vc). a) A mixture of 3 g of 2-carboethoxy-6-(β-carboethoxyethyl)piperidine and 0.82 g of methyl iodide was heated in 11 ml of anhydrous benzene for 6 hours at 40-50° (in a bath). After the reaction mass was cooled, 5 ml of water was added, the mixture was shaken, and the benzene layer was separated. The lower aqueous layer was extracted 2-3 times with 10-15 ml portions of benzene. All the benzene extracts were combined, dried with calcined potassium carbonate, the benzene was distilled off, and the residue was distilled in vacuo. 1.0 g was obtained of a material with b.p. 138-140° (0.2 mm), n_D^{22} 1.4625. It was a colorless, oily material, readily soluble in the usual organic solvents and insoluble in water.

Found %: C 61.91; H 9.04; N 5.22. $C_{14}H_{25}O_4N$. Calculated %: C 61.96; H 9.25; N 5.16.

The aqueous layer was evaporated in vacuo, and the residue was treated with an excess of 50% potassium carbonate solution and extracted with ether. From the extract was obtained 1.2 g of the starting 2-carboethoxy-6-(β-carboethoxyethyl)piperidine with b.p. 152° (0.35 mm). The yield of the methylated product, calculated on the basis of the 2-carboethoxy-6-(β-carboethoxyethyl)piperidine entering into the reaction, was 52.6%.

b) To a suspension of 12.15 g of silver oxide in 45 ml of anhydrous alcohol, in which was dissolved 18 g of 2-carboethoxy-6-(β-carboethoxyethyl) piperidine was added, with cooling, 10 g of methyl iodide. The reaction mass was stirred at room temperature for 8 hours. The precipitate of silver iodide was filtered off, the methyl alcohol was distilled off, and the residue was distilled in vacuo. 10 g (52.8%) was obtained of a colorless, oily liquid with b.p. 138-140° (0.2 mm), n_D^{22} 1.4625.

9-Methyl-2-keto-9-azabicyclo(3,3,1)nonane (VI). 4.37 g of metallic potassium was dispersed in 10 ml of anhydrous toluene. To the hot suspension was added dropwise, with stirring, 5.1 ml of anhydrous alcohol mixed with 16 ml of toluene. At the end of the addition the reaction mixture was boiled for 2 hours. To the hot mixture of potassium alcoholate and toluene that was formed there was added dropwise a solution of 12 g of 2-carboethoxy-6-(β-carboethoxyethyl)-N-methylpiperidine in 30 ml of toluene. As the addition was made, a yellow-brown precipitate separated and the mixture darkened. The mixture was boiled for 3 hours with stirring, then it was cooled to 0° and 65 ml of hydrochloric acid was added drop by drop. The precipitate of potassium chloride that separated was filtered off, the toluene layer was separated and extracted twice with 10 ml portions of hydrochloric acid, the acid extracts were treated with carbon, filtered, and heated on a boiling water bath for 15 hours. Then the solution was evaporated in vacuo. The residue was treated with an excess of 50% potassium carbonate solution and extracted with ether. After drying and removal of the solvent, the residue was distilled in vacuo. 0.76 g (11%) was obtained of a light yellow, mobile liquid with b.p. 92-94° (0.25 mm). The material was very unstable and on storage even in a vacuum desiccator was already converted by the next day to a brown, caramel-like, undistillable mass.

The hydrochloride was an oil.

The picrate formed bright yellow crystals with m.p. 213-215° (from alcohol).

Found %: C 47.25; H 4.76; N 14.77. $C_{15}H_{18}O_8N_4$. Calculated %: C 47.14; H 4.74; N 14.65.

9-Methyl-2-hydroxy-9-azabicyclo(3,3,1)nonane (VII). 0.76 g of 9-methyl-2-keto-9-azabicyclo(3,3,1)-nonane was reduced with 0.3 g of lithium aluminum hydride in ether solution. 0.48 g (63%) was obtained of a colorless, immobile material with b.p. 108° (0.6 mm).

The picrate formed bright yellow crystals from alcohol with m.p. 254° (decomp.).

Found %: C 46.62; H 5.22. $C_{15}H_{20}O_8N_4$. Calculated %: C 46.87; H 5.24.

The hydrochloride formed colorless crystals with m.p. 251.5-252.5°.

Found %: N 7.03, 7.01; Cl 18.73, 18.69. $C_9H_{18}ONCl$. Calculated %: N 7.30; Cl 18.50.

SUMMARY

9-Methyl-2-hydroxy-9-azabicyclo(3,3,1)nonane has been synthesized, starting from 2,6-lutidine.

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INVESTIGATIONS IN THE FIELD OF SUBSTITUTED PHENYLOSAZONES AND PHENYLHYDRAZONES

I. THE EFFECT OF INDIVIDUAL SUBSTITUENTS ON THE INDICATING PROPERTIES OF SOME PHENYLOSAZONES AND PHENYLHYDRAZONES

N. V. Chugreeva

In both our native and the foreign literature, definite attention is paid to the relation between the structure of organic compounds and their indicating properties.

Various azo compounds and indicators of the phthalein series have been subjected to the most detailed investigation by the introduction of different substituents into the benzene ring or the side chain (carbonyl and hydroxyl groups, alkyl radicals, halogens, nitro groups, etc.).

The work of Thiel, Blumberger, and other investigators [1-6] has established the effect of these and other substituents on the intensity and the character of the color, on shifting of the maximum light absorption, and, which is less important, on shifting of the range of shading in comparison with the starting indicators. The rules discovered, as the authors themselves have noted, cannot be considered universal and applicable to any class of indicators. The question of what part of the molecule any substituents should be introduced into depends both on the chemical nature of the substituent and that of the compound developed, and in the final analysis is determined by the requirements set forth for the indicator in each concrete case.

However, some very general rules exist, which were established by Kuznetsov [7] and merit attention for practical use. It is necessary to pay attention to salt- or complex-forming groups capable of producing colored cyclic salts with metal ions, which alter the hue of the indicator itself.

Kuznetsov and Kosheleva [8] published a communication devoted to the question of the relation between the structure and the pH region of the transition of azo indicators of the methyl orange series. Nevertheless, the introduction of substituents into the para-position to the active group, recommended by the authors, can be used, as shown by our investigations, for other classes of organic compounds also, and especially for phenylosazones and phenylhydrazones.

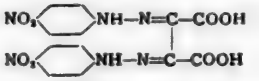
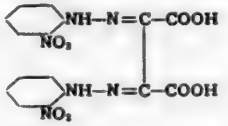
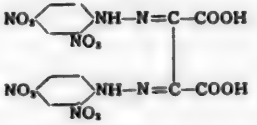
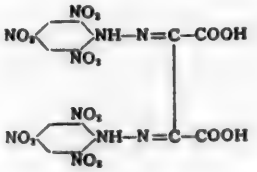
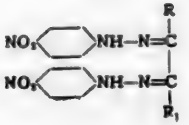
In due time Kuhlberg stated the considerations concerning the necessity of detailed study of some derivatives of the phenylosazone of dihydroxytartaric acid, which were not described in the literature, as possible indicators for high pH values. From this point of view the establishment of a series of rules dependent on the effect of substituents in the molecules of the hydrazones and osazones of carbonyl-containing compounds is absolutely necessary.

In this publication the results are reported of investigations into the effect of the number and position of nitro groups in the benzene ring on the transition range and optical properties of both nitrophenylosazones of dihydroxytartaric acid and a number of other compounds described in the literature and previously used for the indentification of carbonyl-containing compounds. A comparison is made with the properties of some unsubstituted phenylosazones and phenylhydrazones and their bromo derivatives.

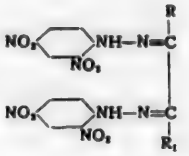
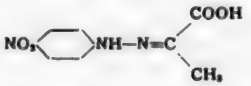
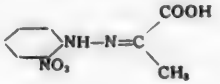
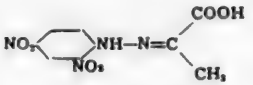
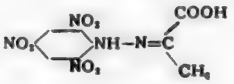
EXPERIMENTAL

The following compounds were synthesized by existing methods [9, 10]: p-nitro-, m-nitro-, o-nitro-, 2,4-dinitro-, and 2,4,6-trinitrophenylosazones of dihydroxytartaric acid; p-nitro-, m-nitro-, o-nitro-, 2,4-di-

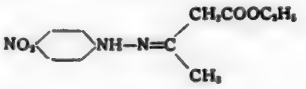
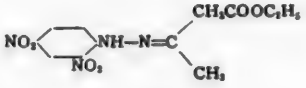
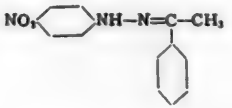
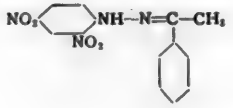
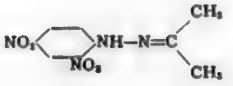
Approximate Transition Range of Indicators of the Hydrazone Series

No.	Name of indicator	Structural formula	Color of form		Transition range in pH values
			acid	alkaline	
1	p-Nitrophenylosazone of dihydroxy-tartaric acid		Light yellow	Light blue	12.6—13.5
2	o-Nitrophenylosazone of dihydroxy-tartaric acid		Light yellow	Rosy orange	4.5— 6.1
3	2,4-Dinitrophenylosazone of dihydroxy-tartaric acid		Light yellow	Light violet	12.3—13.3
4	2,4,6-Trinitrophenylosazone of dihydroxytartaric acid		Yellow Rose Violet	Rose Violet Red-violet	7—9 9—11 11—13
5	p-Nitrophenylosazone of ascorbic acid		Light yellow	Blue-green	11.3—12.6

Continued

No.	Name of indicator	Structural formula	Color of form		Transition range of pH values
			acid	alkaline	
6	2,4-Dinitrophenylosazone of ascorbic acid		Light yellow	Rosy violet	11—12.5
7	p-Nitrophenylhydrazone of pyroracemic acid		Light yellow	Red or dark rose	12—12.9
8	o-Nitrophenylhydrazone of pyroracemic acid		Light yellow	Orange-yellow	4.3—6.1
9	2,4-Dinitrophenylhydrazone of pyroracemic acid		Light yellow	Red or dark rose	11.9—12.9
10	2,4,6-Trinitrophenylhydrazone of pyroracemic acid		Rose Violet Indigo blue	Yellow Rose Violet	6.8— 9 6.8— 9 9 —11 11 —13

Continued

No.	Name of indicator	Structural formula	Color of form		Transition range in pH values
			acid	alkaline	
11	p-Nitrophenylhydrazone of aceto-acetic ester		Light yellow	Rose	11.5—12.7
12	2,4-Dinitrophenylhydrazone of aceto-acetic ester		Light yellow	Rose	11—12.5
13	p-Nitrophenylhydrazone of acetophenone		Yellow	Rose with orange tinge	11.9—12.9
14	2,4-Dinitrophenylhydrazone of acetophenone		Yellow	Pale rose	11.7—12.8
15	2,4-Dinitrophenylhydrazone of acetone		Light yellow	Dark rose	11.6 (11.5)—12.6

nitro-, and 2,4,6-trinitrophenylhydrazones of pyroracemic acid; p-nitro- and 2,4-dinitrophenylhydrazones of acetoacetic ester; 2,4-dinitrophenylhydrazone of acetone; p-nitro- and 2,4-dinitrophenylhydrazones of acetophenone; phenylosazone of dihydroxytartaric acid; phenylhydrazone of pyroracemic acid; and their p-bromo derivatives. The description of these products is the subject of the following report.

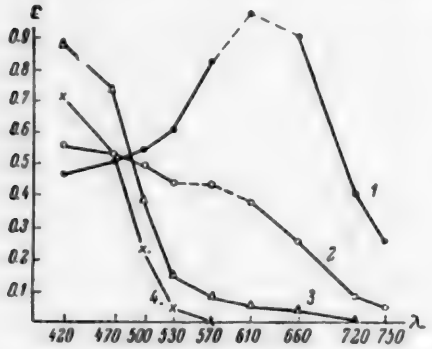


Fig. 1. Light-absorption curves of solutions of p-nitrophenylosazone of dihydroxytartaric acid.
pH values: 1) 13.7, 2) 13.0, 3) 12.0 4) 6.9.

Because of the slight solubility in water of the compounds that were prepared, 0.0005 M alcoholic solutions (optimum concentration) were used for all the experiments.

The possibility of the appearance of indicating properties was checked over a wide range of pH values (from 0 to 14) and the approximate transition intervals were established by a visual method. In this way it was ascertained that the unsubstituted phenylosazones and phenylhydrazones, and the m-nitro and bromo derivatives were not capable of an indicator transformation and at the pH values mentioned above, the colors of their solutions did not change. The results of experimental data on the determination of the transition range are presented in the table (R and R_1 are counterparts of the ascorbic acid molecule).

Since the m-nitro derivatives, the bromine derivatives, and the unsubstituted phenylosazones and phenylhydrazones at all pH values had the same color (pale yellow), they were not included in the table.

From a comparison of the data given in the table, it is clearly evident that the compounds investigated have distinct indicator properties which are subject to definite rules. The most similar in properties (color of alkaline form, magnitude and position of transition range) are the p- and dinitrophenylhydrazones, in which the presence of the aromatic ring of acetophenone has almost no effect on the indicator properties. In the corresponding osazones of dihydroxytartaric acid the transition range lies in the region of higher pH values.

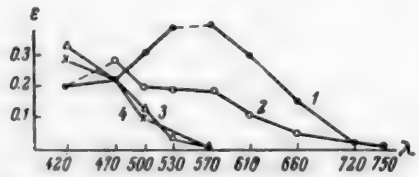
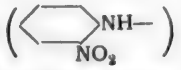


Fig. 2. Light-absorption curves of solutions of 2,4-dinitrophenylosazone of dihydroxytartaric acid.
pH values: 1) 13.7, 2) 13.0, 3) 12.0, 4) 6.9.

A general rule for all the indicators is a small (0.1-0.2 pH units) shift in the transition range toward the lower pH values for the 2,4-dinitro derivatives in comparison with the p-nitro derivatives and a sharp shift into the acid region for the o-nitro derivatives. Furthermore, the introduction of the nitro group in the ortho position in relation to the imine nitrogen  broadens the transition range. As for the trinitro derivatives, here attention is turned to the distinctly expressed three-color transition, and to each stage there corresponds its own transition range, comprising on the average two pH units, with a general shift to the neutral region.

The rules mentioned were confirmed by a study of the light absorption of solutions of the above-enumerated osazones and hydrazones at definite pH values that guarantee the presence of both alkaline and acid forms. Measurements of the optical density were carried out in a Pulfrich photometer with 0.0005 M solutions in a cuvette with a layer thickness of 1 cm.

Since it was not possible to illustrate all of the absorption curves, we have limited ourselves to the consideration of the results obtained for solutions of the p-nitro-, 2,4-dinitro-, o-nitro-, m-nitro-, and p-bromophenylosazones of dihydroxytartaric acid and the unsubstituted phenylosazone (Figs. 1-6).

Analysis of the light-absorption curves shows that introduction of a nitro group in the para-position to the

imine nitrogen is accompanied in the alkaline form of the indicator by a clearly expressed bathochromic and hyperchromic effect (Fig. 1). When two nitro groups are present (in the para- and ortho-position) the maximum light absorption for the alkaline form is shifted a little to the shorter-wave part of the spectrum (Fig. 2), with a simultaneous decrease in the intensity of light absorption.

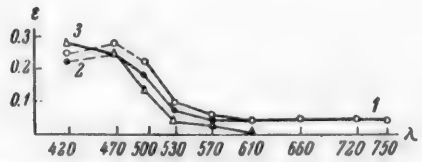


Fig. 3. Light-absorption curves of solutions of o-nitrophenylosazone of dihydroxytartaric acid.
pH values: 1) 13.0, 2) 6.9, 3) 3.5.

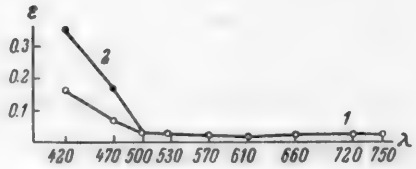


Fig. 4. Light-absorption curves of solutions of m-nitrophenylosazone of dihydroxytartaric acid.
pH values: 1) 13, 2) 6.9.

Introduction of a nitro group in the ortho position leads at the same time to a sharply expressed hypsochromic effect and a decrease in intensity of light absorption (Fig. 3). In fact, the identical course of the curves for the solutions of the remaining three osazones (Figs. 4-6) conforms with the absence in these compounds of indicator properties.

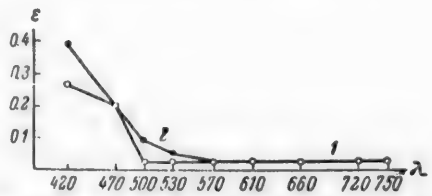


Fig. 5. Light-absorption curves of solutions of p-bromophenylosazone of dihydroxytartaric acid.
pH values: 1) 13.0, 2) 6.9.

Fig. 6. Light-absorption curves of solutions of phenylosazone of dihydroxytartaric acid.
pH values: 1) 13.0, 2) 6.9.

The present work was carried out under the direction of L. M. Kuhlberg.

SUMMARY

1. As a result of an investigation of a series of phenylosazones and hydrazones, it has been established that the presence of nitro groups in the benzene ring in a definite position – ortho, para, or simultaneously in both positions – communicates to these compounds clearly expressed indicator properties.

2. Introduction of a nitro group in the ortho position shifts the transition range to the acid region; introduction of the same group in the para position leads to a shift of the transition range to the region of high pH values.

Accumulation of a number of nitro groups, in turn, causes a shift in the transition range to the region of low pH values.

3. It has been shown that the transformation of the acid form of the compounds studied to the alkaline form is accompanied by a bathochromic effect, which is especially clearly expressed in the p-nitrophenylosazone of dihydroxytartaric acid.

4. Introduction of bromine into the benzene ring does not communicate indicator properties to the phenylosazones and phenylhydrazones.

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* In Russian.

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STRUCTURE AND REACTIVITY OF AROMATIC HYDROCARBONS

II. THE AZO-COUPLING REACTION OF PHENYLATED ETHYLENES WITH p-NITRODIAZOBENZENE HYDROCHLORIDE

V. V. Razumovsky and E. F. Rychkina

When 1,1-diphenylethylene is reacted with p-nitrodiazobenzene hydrochloride in pyridine solution, two compounds are formed – 1,1-diphenyl-2-p-nitrophenylethylene and p-nitrobenzyldiphenylcarbinol [1].

Upon further investigation of this reaction in acetic acid solution it has been found that nitrogen is not given off and that azo-coupling takes place with the formation of 1,1-diphenyl-2,2-di(p-nitrobenzeneazo)ethylene (I).

$$(C_6H_5)_2C{=}C(N_2C_6H_4NO_2)_2$$
(I)

As evidence of the fact that the substance obtained was actually the bisazo compound, it was reduced with stannous chloride in the presence of hydrochloric acid. In the reduction products was found p-phenylenediamine, which was identified by conversion to quinonedichloroimine.

We further conducted experiments investigating the reaction of other phenylated ethylenes (1,1-diphenylpropene-1, 2-phenylpropene, styrene, stilbene, triphenylethylene) with p-nitrodiazobenzene hydrochloride.

When 1,1-diphenylpropene-1 was reacted with p-nitrodiazobenzene hydrochloride in pyridine solution, evolution of nitrogen occurred and two compounds were obtained – 1,1-diphenyl-2-p-nitrophenylpropene-1 (II) and 1,1-diphenyl-2-p-nitrophenylpropanol-1 (III).

The structure of 1,1-diphenyl-2-p-nitrophenylpropene-1 was demonstrated by oxidation to benzophenone and p-nitrobenzoic acid.

The formula of 1,1-diphenyl-2-p-nitrophenylpropanol was assigned to the second product on the basis of the fact that on treatment in the cold with 30% sulfuric acid it was converted into 1,1-diphenyl-2-p-nitrophenylpropene-1

$$(C_6H_5)_2COH{-}CH\begin{matrix}CH_3\\C_6H_4NO_2\end{matrix} \longrightarrow (C_6H_5)_2C{=}C\begin{matrix}CH_3\\C_6H_4NO_2\end{matrix}$$
(III) (II)

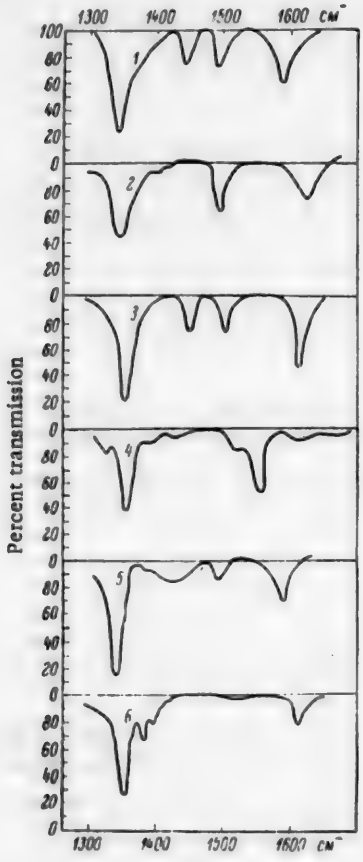
The complete analogy between the products formed in pyridine solutions by the reaction of unsym. diphenylethylene and of 1,1-diphenylpropene-1 with p-nitrodiazobenzene hydrochloride should be pointed out.

When the reaction was carried out between equimolecular quantities of these reagents in acetic acid, a bright red substance was obtained that melted with decomposition at 176°, investigation of which was very difficult because of its extreme instability. According to data from the analysis for nitrogen, we might ascribe to it the formula

$$(C_6H_5)_2C{=}C\begin{matrix}CH_3\\N{=}N{-}C_6H_4NO_2\end{matrix}$$
(IV)

1,1-diphenyl-2-(p-nitrobenzeneazo)propene-1 (IV). It was possible to obtain by purification of the latter only a trifling amount of pure 1,1-diphenyl-2-(p-nitrobenzeneazo)propene-1 (IV).

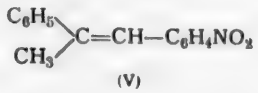
When the reaction between the 2-phenylpropene (V) and p-nitrodiazobenzene hydrochloride was carried out in pyridine solution, it was not possible to identify the individual material.



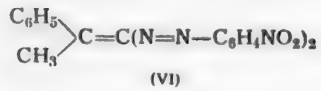
Infrared spectra of products of azo-coupling and arylation of phenylated ethylenes.

1) 1,1-Diphenyl-2-p-nitrophenylethylene [1], 2) 1,1-diphenyl-2,2-di(p-nitrobenzeneazo)ethylene (I), 3) 1,1-diphenyl-2-p-nitrophenylpropene-1 (II), 4) 1,1-diphenyl-2-(p-nitrobenzeneazo)propene-1 (IV), 5) 1-p-nitrophenyl-2-phenylpropene-1 (V), 6) unsym. di(p-nitrobenzeneazo)methylphenylethylene (VI).

In acetic acid solution we obtained two products – unsym. di(p-nitrobenzeneazo)methylphenylethylene (VI) and 1-p-nitrophenyl-2-phenylpropene-1 (V).



(V)



(VI)

When reduction of (VI) was carried out with stannous chloride in alcohol solution, p-phenylenediamine was found. The reduction products of the other part of the molecule were not isolated.

Upon oxidation of (V) with potassium permanganate, acetophenone and p-nitrobenzoic acid were obtained.

Under similar conditions we carried out experiments in different media between p-nitrodiazobenzene hydrochloride and styrene, stilbene, and triphenylethylene. In not one of the numerous instances were we able to isolate specific reaction products. At the same time, it is known that it is possible by the use of catalysts to carry out a reaction of styrene with diazonium salts [2].

We explain the negative result in the case of styrene (in the absence of a catalyst) by the fact that polarization of the double bond with one phenyl group is insufficient to accomplish the reaction with p-nitrodiazobenzene. With the simultaneous effect of two phenyl groups in the molecule of unsym. diphenylethylene or 1,1-diphenylpropene-1, polarization of the double bond is brought about to a more considerable extent and is sufficient for reaction with p-nitrodiazobenzene to take place. In sym. diphenylethylene (stilbene) and triphenylethylene the phenyl groups act against each other in their polarizing effect on the ethylenic bond. We explained in this way the negative result in carrying out the reaction of stilbene and triphenylethylene with p-nitrodiazobenzene hydrochloride.

For the purpose of confirming the proposed structure, we investigated the infrared spectra for six materials described in this and the preceding [1] communications in the interval 1300-1650 cm^{-1} * (figure).

In all the spectra the characteristic intensive frequency of the nitro group around 1350 cm^{-1} was found. The second frequency that usually appears in the spectra of nitro compounds (around 1500 cm^{-1}) was considerably less intense, especially in the spectrum of compound (V). The problem of the characteristic frequencies of the azo group is still not finally resolved. A number of investigators ascribe to the azo group a frequency around 1580 cm^{-1} [3].

* Spectra were taken with an IKS-6 spectrograph with NaCl prism in 5% CCl_4 solution.

In the spectra of the azo compounds obtained by us only compound (IV) had two frequencies in the region 1500-1580 cm^{-1}. In this case the lower frequency could be ascribed to the nitro group, and the higher to the azo group. In all other cases the absorption caused by the azo group apparently was superimposed on the frequency of the nitro group or of the aromatic ring.

Thus the infrared spectra could not be used as an especially weighty argument in favor of the proposal previously expressed by us concerning the structure of the compounds obtained.

EXPERIMENTAL

Reaction of unsym. diphenylethylene with p-nitrodiazobenzene hydrochloride in acetic acid medium. p-Nitroaniline was diazotized in a mixture of equal volumes of concentrated hydrochloric acid and glacial acetic acid with a small excess of nitrite. The unreacted nitrous acid was decomposed by the addition of urea. To a solution of unsym. diphenylethylene in glacial acetic acid was added with continuous stirring the calculated amount of the solution of p-nitrodiazobenzene hydrochloride in glacial acetic acid. The reaction mixture stood until a qualitative test with H-acid for the presence of the diazonium salt began to give a negative result. The reaction mixture, which was a dark brown liquid, was extracted with ether. The ether extract was washed with a dilute solution of sodium carbonate and dried with granular calcium chloride. The red-brown oil remaining after the ether was distilled off crystallized partially after prolonged standing. The dark red material separated by filtration was recrystallized repeatedly from methyl alcohol and acetone. After recrystallization dark red crystals of 1,1-diphenyl-2,2-di(p-nitrobenzeneazo) ethylene (I) were obtained, which melted at 225° (decomp.). The compound dissolved in acetone, ethyl acetate, and ethyl alcohol, and slightly in glacial acetic acid, benzene, petroleum ether, and carbon tetrachloride; it was insoluble in water.

Found %: C 65.49, 65.60; H 4.02, 3.92; N 17.42, 17.59. $C_{26}H_{18}O_4N_6$. Calculated %: C 65.27; H 3.78; N 17.57.

Upon reduction with stannous chloride in alcohol solution in the presence of hydrochloric acid, phenylenediamine was obtained, which was identified by its conversion by the action of a solution of calcium hypochlorite to quinonedichloroimine with m.p. 124° (decomp.), giving no lowering in melting point with quinonedichloroimine obtained from a known preparation of p-phenylenediamine.

Reaction of 1,1-diphenylpropene-1 with p-nitrodiazobenzene hydrochloride. 1,1-Diphenylpropene-1 was prepared by dehydration of ethyldiphenylcarbinol synthesized by the reaction of ethylmagnesium bromide with benzophenone. The compound melted at 48.5° (ethyl alcohol), which agrees with the literature data [4].

a) In pyridine solution. To a solution of 1,1-diphenylpropene-1 in pyridine there was added with continuous stirring the calculated amount of an aqueous solution of p-nitrodiazobenzene hydrochloride. The reaction mixture took on a red color, which then changed to reddish brown. The temperature of the reaction mixture spontaneously rose to 40-45° (without external cooling). The reaction mixture was left overnight. In the morning the precipitate was filtered off and from it after repeated recrystallization from ethyl acetate there were obtained light yellow crystals of 1,1-diphenyl-2-p-nitrophenylpropene-1 (II). M.p. 192.5°, yield 8-9%. The compound was readily soluble in benzene and boiling ethyl alcohol, in glacial acetic acid and ethyl acetate upon heating, and was slightly soluble in ethyl ether, petroleum ether, and methyl alcohol, and completely insoluble in water.

Found %: C 79.96, 80.18; H 5.57, 5.39; N 4.41, 4.58. M 312.3, 316.3. $C_{21}H_{17}O_2N$.
Calculated %: C 80.0; H 5.47; N 4.40. M 315.

As evidence of the structure of the compound it was oxidized with potassium permanganate in water-pyridine solution, first at room temperature and then at 40-45°. As a result of oxidation, benzophenone and p-nitrobenzoic acid were obtained. The benzophenone was identified through its 2,4-dinitrophenylhydrazone, which melted at 238° and gave no depression in melting point with known 2,4-dinitrophenylhydrazone of benzophenone. The p-nitrobenzoic acid (m.p. 240°) gave no lowering of the melting point when mixed with known p-nitrobenzoic acid.

After separation of the 1,1-diphenyl-2-p-nitrophenylpropene-1, the calculated amount of dilute hydrochloric acid was added to the filtrate (to tie up the pyridine) and ether extraction was carried out. The brown oil obtained after the ether was distilled off crystallized upon prolonged standing. By repeated recrystallization from ethyl alcohol a colorless, crystalline substance with a yellowish tinge was obtained with m.p. 184°. The compound was

soluble in ethyl acetate and boiling ethyl alcohol; slightly soluble in sulfuric acid, petroleum ether, and carbon tetrachloride, and insoluble in water; it revealed the presence of a hydroxyl group (reaction with methylmagnesium iodide). According to the analytical data, the compound corresponded to 1,1-diphenyl-2-p-nitrophenylpropanol (III).

Found %: C 75.40, 75.59; H 5.89; 5.79; N 4.16, $C_{21}H_{19}O_3N$. Calculated %: C 75.67; H. 5.77; N 4.20.

Upon treatment of the compound (III) with 30% sulfuric acid at room temperature, splitting out of water occurred, accompanied by considerable tar formation. By extraction of this solution with ether, 1,1-diphenyl-2--p-nitrophenylpropene-1 (II) was obtained with m.p. 192.5°.

b) In acetic acid solution. To an acetic acid solution of 1,1-diphenylpropene-1 there was added gradually, with continuous stirring, the calculated amount of an acetic acid solution of p-nitrodiazobenzene hydrochloride. The reaction mixture (a dark red liquid with a tarry precipitate) was allowed to stand at room temperature until the qualitative reaction for the diazonium salt disappeared. The stirrer operated intermittently. The filtrate that was filtered off was treated several times with ether while heating. From the portion insoluble in ether there was separated a small amount of an unstable, red material with m.p. 176°, corresponding, apparently, to 1,1-diphenyl-2-(p-nitrobenzeneazo)propene-1 (IV). The compound dissolved in chloroform, glacial acetic acid, and methyl alcohol.

Found %: N 12.28, 12.00. $C_{21}H_{17}O_2N_3$. Calculated %: N 12.24.

Investigation of the product is continuing.

Reaction of 2-phenylpropene with p-nitrodiazobenzene hydrochloride. 2-Phenylpropene was prepared by the dehydration of dimethylphenylcarbinol, synthesized by the reaction of phenylmagnesium bromide with acetone, and was an oily liquid with b.p. 160-161° [5].

When the reaction was carried out between equimolecular amounts of the compounds named in the heading in pyridine solution under the conditions described previously for 1,1-diphenylpropene-1, it was not possible to isolate the individual reaction products because of tarring of the reaction mass and the difficulty of separating the mixture obtained.

To an acetic acid solution of 2-phenylpropene there was added with continuous stirring the calculated amount of an acetic acid solution of p-nitrodiazobenzene hydrochloride. Then the mixture was allowed to stand at room temperature until the reaction for diazonium salt disappeared. Stirring was carried on intermittently. The mixture obtained separated into two layers: the lower one was a thick oil, the upper a light brown solution. The two layers were treated separately with ether. From the lower, oily layer the ether-insoluble unsym. di(p-nitrobenzeneazo)--methylphenylethylene (VI) was isolated. After repeated recrystallization from acetone a light red material was obtained with a characteristic silvery luster. The yield was about 10%. The compound dissolved in benzene, dichloroethane, methyl alcohol, and glacial acetic acid, and was slightly soluble in ethyl and petroleum ether; it was insoluble in water.

Found %: C 60.8; H 3.83; N 19.62, 19.62. $C_{21}H_{16}O_4N_6$. Calculated %: C 60.58; H 3.85; N 20.19.

In order to demonstrate that the compound was actually the bis-azo compound, it was reduced with stannous chloride in alcohol solution in the presence of hydrochloric acid. The tin was separated electrolytically from the solution that was obtained, after which the filtrate was evaporated to dryness in vacuo (with a water-jet pump). p-Phenylenediamine was isolated from the residue and identified as quinonedichloroimine with m.p. 124° (decomp.) (mixed m.p. test).

From the ether solution of the lower layer after separation of the ether-insoluble unsym. di(p-nitrobenzeneazo)methylphenylethylene (VI) there was obtained a thick, dark brown oil, which crystallized after prolonged standing. By repeated recrystallization from petroleum ether light yellow crystals of 1-p-nitrophenyl-2-phenylpropene-1 (V) were obtained with m.p. 106°. The compound dissolved in petroleum ether, methyl alcohol, ethyl alcohol, and glacial acetic acid.

Found %: C 75.18, 75.40; H 5.39, 5.46; N 6.11. M 250.5, 252. $C_{15}H_{13}O_2N$. Calculated %: C 75.31; H 5.44; N 5.85. M 239.

As evidence of the structure of the compound it was oxidized with an aqueous solution of potassium per-

manganate. In the oxidation products were found acetophenone (semicarbazone, m.p. 198°) and p-nitrobenzoic acid (m.p. 240°).

SUMMARY

1. It has been established that 1,1-diphenyl-2,2-di(p-nitro benzeneazo)ethylene is obtained by the reaction of 1,1-diphenylethylene with p-nitrodiazobenzene hydrochloride in acetic acid solution.

2. It has been shown that 1,1-diphenylpropene-1 with p-nitrodiazobenzene hydrochloride in pyridine solution yields 1,1-diphenyl-2-p-nitrophenylpropene-1 and 1,1-diphenyl-2-p-nitrophenylpropanol, but in acetic acid solution the extremely unstable 1,1-diphenyl-2-(p-nitrobenzeneazo)propene-1 is obtained.

3. It has been found that when 2-phenylpropene is reacted with p-nitrodiazobenzene hydrochloride in acetic acid solution, two reaction products are obtained — 1-p-nitrophenyl-2-phenylpropene-1 and unsym. di(p--nitrobenzeneazo)methylphenylethylene.

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ETHYLENE SULFIDE IN THE SYNTHESIS OF HETEROCYCLIC COMPOUNDS WITH TWO HETEROATOMS

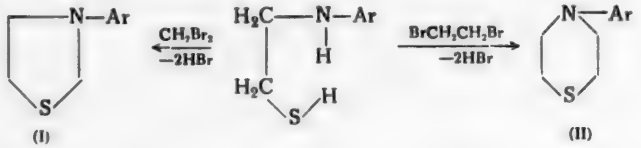
IV. SYNTHESIS OF 3-ARYLTHIAZOLIDINES AND 4-ARYLTHIAZANES-1,4

Yu. K. Yuryev and S. V. Dyatlovitskaya

In a previous communication [1] we have shown that N-(β-mercaptoethyl) arylamines readily react with the acid chloride of carbonic acid, giving 3-arylthiazolidones-2 in yields of 50-90%. In connection with this it was of interest to study the behavior of N-(β-mercaptoethyl)arylamines in a similar reaction with dihalides containing less active halogen atoms than phosgene, and especially with alkyl 1,1- or 1,2-dihalides. In the literature it is indicated [2] that ethylene bromide has been used for condensation with β-aminoethylmercaptan but thiazane-1,4-was formed in this reaction, apparently, only in insignificant yield.

When N-(β-mercaptoethyl)arylamines (like β-aminoethylmercaptan itself) are reacted with methylene bromide and ethylene bromide, condensations with the splitting out of two molecules of hydrogen halide may proceed in several directions, since the splitting out of two atoms of hydrogen from N-(β-mercaptoethyl)arylamines (from the amine and the sulfhydryl groups) is theoretically possible by the following four routes, which should lead to reaction products of different natures.

a) Splitting out of hydrogen atoms from the amine and sulfhydryl groups of a molecule of N-(β-mercaptoethyl)arylamine upon condensation with a molecule of methylene bromide or ethylene bromide should lead to the formation of 3-arylthiazolidines (I) or 4-arylthiazanes-1,4 (II):



(I) (II)

b) Splitting out of hydrogen atoms from the sulfhydryl groups of two molecules of N-(β-mercaptoethyl)arylamines upon condensation with a molecule of methylene bromide or ethylene bromide should lead to the formation of the corresponding sulfides $ArHNCH_2CH_2S(CH_2)_nSCH_2CH_2NHAr$ (n = 1,2).

c) Splitting out of hydrogen atoms from the amine groups of two molecules of N-(β-mercaptoethyl)arylamines upon condensation with a molecule of methylene bromide or ethylene bromide should lead to the formation of the corresponding dithiols

$$HSCH_2CH_2(Ar)N(CH_2)_nN(Ar)CH_2CH_2SH \quad (n = 1,2).$$

d) Splitting out of hydrogen atoms from the amine and sulfhydryl groups of two molecules of N-(β-mercaptoethyl)arylamines upon condensation with a molecule of methylene bromide or ethylene bromide should lead to the formation of the mercaptosulfide $HSCH_2CH_2(Ar)N(CH_2)_nSCH_2CH_2NHAr$ (n = 1,2).

An investigation of the reaction of N-(β-mercaptoethyl)arylamines with methylene bromide and ethylene bromide, carried out in the present work, showed that actually the condensation proceeded predominantly according to the first of the indicated routes, and 38-51% yields were obtained of the 3-arylthiazolidines and the 4-arylthiazanes-1,4. In this way, by the reaction of N-(β-mercaptoethyl)aniline, -o- and -p-toluidine, and -o- and

-p-anisidine with methylene bromide we obtained 3-phenyl-, 3-o-tolyl-, 3-p-tolyl-, 3-o-anisyl-, and 3-p-anisylthiazolidine, and by reaction with ethylene bromide we obtained 4-phenyl-, 4-p-tolyl-, 4-o-anisyl-, and 4-p-anisylthiazane-1,4.

Along with these rather easily separated reaction products we obtained from the residue oils that gave a positive reaction for the sulfhydryl group. When they were distilled in vacuo, they boiled over wide ranges and underwent strong decomposition, and they therefore were not investigated more closely.

Thus, reactions by the other indicated routes also occurred and led to the formation of a complex mixture of materials that contained noncyclically bound nitrogen and sulfur atoms. According to the data in the literature [3], such noncyclic condensation products are formed on the reaction of aromatic amines with β,β'-dichlorodiethyl sulfide, when along with thiazanes-1,4, aminosulfides $(ArHNCH_2CH_2)_2S$ also are obtained that are formed as a result of the splitting out of hydrogen from two amino groups by a reaction proceeding at a molar ratio of the reactants of 1 : 2.

Condensation of N-(β-mercaptoethyl)arylamines with alkyl-1,2-dihalides containing secondary halogen atoms, such as 1,2-dibromocyclohexane and 2,3-dibromobutane, does not take place; the corresponding thiazanes-1,4 are not formed, and the arylaminomercaptans are recovered from the reaction unchanged. The cause of this, apparently, is the great activity of the halogen atoms, which explains the easy intramolecular splitting out of hydrogen halide in the alcoholic alkali medium, in which the condensations described by us were carried out.

EXPERIMENTAL

1. Synthesis of 3-arylthiazolidines

3-Phenylthiazolidine. 3.8 g of N-(β-mercaptoethyl)aniline in 25 ml of anhydrous alcohol was boiled for 4 hours on a water bath with 5 g of methylene bromide, 2.5 g of anhydrous sodium acetate, and 3.5 g of anhydrous sodium carbonate. Then the alcohol was distilled off, water was added until the salt dissolved, and the reaction product was repeatedly extracted with ether. The ether extracts were dried with anhydrous magnesium sulfate. After the ether was distilled off, distillation of the oily residue in vacuo in a current of nitrogen yielded a fraction with b.p. 159-161° (11 mm), which crystallized upon standing. The crystals were separated out and recrystallized from dilute alcohol. 1.93 g (46%) of 3-phenylthiazolidine was obtained; m.p. 31-32° (from 80% alcohol). A mixed melting point test with known 3-phenylthiazolidine showed no depression [4].

3-p-Tolylthiazolidine. A mixture of 4.17 g of N-(β-mercaptoethyl)-p-toluidine in 25 ml of anhydrous alcohol, 5 g of methylene bromide, 2.5 g of anhydrous sodium acetate, and 3.5 g of anhydrous sodium carbonate was boiled and treated as described above. 2.27 g (50%) of 3-p-tolylthiazolidine was obtained; m.p. 79-80° (from 80% alcohol). A mixed melting point test with known 3-p-tolylthiazolidine showed no depression [4].

3-o-Tolylthiazolidine. A mixture of 8.35 g of N-(β-mercaptoethyl)-o-toluidine in 50 ml of anhydrous alcohol, 10 g of methylene bromide, 5 g of anhydrous sodium acetate, and 7 g of anhydrous sodium carbonate was boiled and treated as described above. An oil was obtained that did not crystallize on prolonged standing. When it was distilled in vacuo in a current of nitrogen, the following fractions were separated: 1) 144-149° (10 mm), 3.4 g; 2) 149-200° (10 mm), 2.2 g (gave positive reaction for the sulfhydryl group).

The 1st fraction was 3-o-tolylthiazolidine, which after a second distillation (yield 38%) had the following constants:

B.p. 147.5-148.5° (10 mm); n_D^{20} 1.5980, d_4^{20} 1.1192; MR_D 54.63; Calc. 54.49.

Found %: C 66.89, 66.96; H 7.55, 7.52; N 8.16, 8.36. $C_{10}H_{13}NS$. Calculated %: C 66.99; H 7.31; N 7.82.

3-p-Anisylthiazolidine. From 4.6 g of N-(β-mercaptoethyl)-p-anisidine in 25 ml of anhydrous alcohol, 5 g of methylene bromide, 2.5 g of anhydrous sodium acetate, and 3.5 g of anhydrous sodium carbonate treated by the above method was obtained 2.54 g (51%) of 3-p-anisylthiazolidine; m.p. 84-85° (from 80% alcohol). A mixed melting point test with known 3-p-anisylthiazolidine showed no depression [4].

3-o-Anisylthiazolidine. A mixture of 9.15 g of N-(β-mercaptoethyl)-o-anisidine in 50 ml of anhydrous alcohol, 10 g of methylene bromide, 5 g of anhydrous sodium acetate, and 7 g of anhydrous sodium carbonate was boiled and treated as described above. An oil was obtained that did not crystallize on standing. When it was dis-

stilled in vacuo the following fractions were separated: 1st 142-144° (2 mm), 4.6 g; 2nd 144-178° (2mm), 1.9 g (gave positive reaction for the sulfhydryl group).

The 1st fraction was 3-o-anisylthiazolidine, which after redistillation (yield 47%) had the following constants:

b.p. 143-144° (2 mm); n_D^{20} 1.6010; d_4^{20} 1.1759; MR_D 56.89; calc. 56.13.

Found %: N 7.46; 7.57. $C_{10}H_{13}ONS$. Calculated %: N 7.17.

3-o-Anisylthiazolidine hydrochloride: m.p. 139-140° (from alcohol).

Found %: N 5.89, 5.71. $C_{10}H_{14}ONClS$. Calculated %: N 6.04.

II. Synthesis of 4-arylthiazanes-1,4

4-Phenylthiazane-1,4. A mixture of 15.3 g of N-(β-mercaptoethyl)aniline in 100 ml of anhydrous alcohol, 22.5 g of ethylene bromide, 10 g of anhydrous sodium acetate, and 14 g of anhydrous sodium carbonate was boiled for 5 hours on a water bath. Then the alcohol was distilled off, water was added until the salt completely dissolved, the solution was extracted repeatedly with ether, and the ether extract was dried with anhydrous potassium carbonate. After the ether was distilled off, distillation of the residue in vacuo in a current of nitrogen yielded the following fractions: 1st 45° (5 mm), 1.3 g (unchanged ethylene bromide); 2nd 138-141° (5 mm), 9.7 g; 3rd 167-174° (5 mm), 4.5 g (gave a positive reaction for a sulfhydryl group).

The 2nd fraction crystallized upon standing and was 4-phenylthiazane-1,4: m.p. 34° (from alcohol) [3, 5-7]. Yield 54%.

Found %: N 7.64, 7.85. $C_{10}H_{13}NS$. Calculated %: N. 7.81.

4-p-Tolylthiazane-1,4. A mixture of 8.35 g of N-(β-mercaptoethyl)-p-toluidine in 50 ml of anhydrous alcohol, 11.25 g of ethylene bromide, 5 g of anhydrous sodium acetate, and 7 g of anhydrous sodium carbonate was boiled and then treated as described above. By distillation of the reaction product in vacuo in a current of nitrogen the following fractions were obtained: 1st 132-133° (3 mm), 4.55 g; 2nd 133-182° (3 mm), 3.1 g (gave a positive reaction for a sulfhydryl group). The 1st fraction, which crystallized upon standing, was 4-p--tolylthiazane-1,4: m.p. 32.5-33° (from alcohol) [3, 7]. Yield 52%.

Found %: N 7.39, 7.23. $C_{11}H_{15}NS$. Calculated %: N 7.25.

4-p-Anisylthiazane-1,4. A mixture of 9.15 g of N-(β-mercaptoethyl)-p-anisidine in 50 ml of anhydrous alcohol, 11.25 g of ethylene bromide, 5 g of anhydrous sodium acetate, and 7 g of anhydrous sodium carbonate was boiled and then treated as described above. The residue obtained after the ether was distilled off crystallized and was 4-p-anisylthiazane-1,4: m.p. 76-76.5° (from alcohol) [3, 7]. Yield 5.4 g (51%).

Found %: N 6.95, 7.09. $C_{11}H_{15}ONS$. Calculated %: N 6.69.

4-o-Anisylthiazane-1,4. A mixture of 9.15 g of N-(β-mercaptoethyl)-o-anisidine in 50 ml of anhydrous alcohol, 11.25 g of ethylene bromide, 5 g of anhydrous sodium acetate, and 7 g of anhydrous sodium carbonate was boiled and then treated as described above. By distillation of the reaction product in vacuo in a current of nitrogen the following fractions were obtained: 1st 145-148° (3 mm), 3.7 g; 2nd 178-203° (3 mm), 3.1 g (gave a positive reaction for a sulfhydryl group). The 1st fraction, which crystallized upon standing, was 4-o-anisylthiazane-1,4: m.p. 51° (from alcohol) [3]. Yield 39.5%.

Found %: N 6.66, 6.75. $C_{11}H_{15}ONS$. Calculated %: N 6.69.

SUMMARY

1. The condensation of N-(β-mercaptoethyl)aniline, N-(β-mercaptoethyl)-p-toluidine, N-(β-mercaptoethyl)-o-toluidine, N-(β-mercaptoethyl)-p-anisidine, and N-(β-mercaptoethyl)-o-anisidine with methylene bromide leads to the formation of the thiazolidine ring and the production, correspondingly, of 3-phenyl-, 3-p-tolyl, 3-p-anisyl- and the previously undescribed 3-o-tolyl- and 3-o-anisylthiazolidine.

2. The condensation of N-(β-mercaptoethyl)aniline, N-(β-mercaptoethyl)-p-toluidine, N-(β-mercaptoethyl)-o-anisidine, and N-(β-mercaptoethyl)-p-anisidine with ethylene bromide leads to the formation of the thiazane-1,4 ring and the production, correspondingly, of 4-phenyl-, 4-p-tolyl-, 4-o-anisyl, and 4-p-anisylthiazane-1,4.

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ETHYLENE SULFIDE IN THE SYNTHESIS OF HETEROCYCLIC COMPOUNDS WITH TWO HETERO ATOMS

V. SYNTHESIS OF 3-ARYLTHIAZOLIDINETHIONES-2

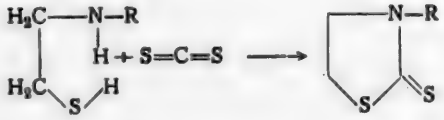
Yu. K. Yuryev and S. V. Dyatlovitskaya

In our previous publications it has been shown that N-(β-mercaptoethyl)arylamines easily condense with aldehydes, phosgene, methylene bromide, and ethylene bromide, giving respectively the 2-alkyl-(or aryl-)-3--arylthiazolidines [1, 2], 3-arylthiazolidones-2 [3], 3-arylthiazolidines, and 4-arylthiazanes-1,4 [4].

However, the N-(β-mercaptoethyl)arylamines might be used also not only in condensations with the splitting out of water or hydrogen chloride or bromide, as occurs in the above-cited instances, but in condenstions with the splitting out of hydrogen sulfide, for example by reaction with carbon bisulfide, which should lead to the formation of 3-arylthiazolidinethiones-2.

Of the compounds of the thiazolidinethione-2 group the more thoroughly studied representatives are those that do not have substituents on the nitrogen atom, and the 3-alkyl-(or aryl-)-thiazolidinethiones-2 have been little investigated, although they have been prepared by means of the following reactions: a) by reaction of 3--arylthiazolidinimines-2 with carbon bisulfide [5-9]; b) by the action of carbon bisulfide on alkynamines [10, 11]; c) by the reaction of N-substituted ethanolamines with carbon bisulfide [10]; d) by the condensation of dibromoethane, a primary amine, and carbon bisulfide [12].

In the present work we have accomplished the condensation of N-(β-mercaptoethyl)arylamines with carbon bisulfide, which proceeded smoothly enough in alcoholic alkali medium and led to the formation of 3-arylthiazolidinethiones-2, which convincingly indicates the high reactivity of the β-aminomercaptans arylated on the nitrogen that we employed in the reaction.



R = C_6H_5; o-$CH_3C_6H_4$; p-$CH_3C_6H_4$; o-$CH_3OC_6H_4$; p-$CH_3OC_6H_4$.

By the action of mercuric oxide [9] on the 3-arylthiazolidinethiones-2 thus obtained, they were converted to the corresponding 3-arylthiazolidones-2, which proved their structure.

It should be noted that N-(β-mercaptoethyl)-o-toluidine and N-(β-mercaptoethyl)-o-anisidine reacted with carbon bisulfide only to a small extent and the yields of thiazolidinethiones obtained from them were low (31% and 5.5% respectively), while in the case of their p- isomers the yields amounted to 70-83% of theoretical. We also noted earlier that the condensation of N-(β-hydroxyethyl)-o-toluidine [13] and N-(β-mercaptoethyl)--o-carbomethoxyaniline [2] with aldehydes and the condensation of N-(β-mercaptoethyl)-o-toluidine with phosgene [3] took place with small yields.

EXPERIMENTAL

Preparation of 3-arylthiazolidinethiones-2

Methods. To 0.02 g-moles of N-(β-mercaptoethyl)arylamine, dissolved in 10 ml of anhydrous alcohol,

were added 1.12 g (0.02 g-mole) of potassium hydroxide and 3.04 g (0.04 g-mole) of carbon bisulfide, and the mixture was boiled for 8 hours. At the end of the heating period the excess carbon bisulfide and alcohol were distilled off. The crystallized residue which was orange in color and was 3-arylthiazolidinethione-2, was transferred onto a porous filter, washed with cold water until colorless, dried in a vacuum desiccator, and recrystallized from alcohol.

3-Phenylthiazolidinethione-2. From 3.06 g of N-(β-mercaptoethyl)-aniline, 3.04 g of carbon bisulfide, and 1.12 g of potassium hydroxide was obtained 3.05 g (78%) of 3-phenylthiazolidinethione-2; m.p. 133-134° (from alcohol).

Found %: C 55.17, 55.11; H 4.78, 4.63; N 7.42, 7.45. $C_9H_9NS_2$. Calculated %: C 55.35; H 4.64; N 7.17.

Literature data for 3-phenylthiazolidinethione-2: m.p. 134° [5]; 128° [8].

3-p-Tolylthiazolidinethione-2. From 3.34 g of N-(β-mercaptoethyl)-p-toluidine, 3.04 g of carbon bisulfide, and 1.12 g of potassium hydroxide was obtained 3.45 g (83%) of 3-p-tolylthiazolidinethione-2; m.p. 126.5-127° (from alcohol).

Found %: N 6.79, 7.04. $C_{10}H_{11}NS_2$. Calculated %: N 6.69.

Literature data for 3-p-tolylthiazolidinethione-2: m.p. 126° [6].

3-o-Tolylthiazolidinethione-2. From 3.34 g of N-(β-mercaptoethyl)-o-toluidine, 3.04 g of carbon bisulfide, and 1.12 g of potassium hydroxide was obtained an oil that partially crystallized upon long standing. The crystals were separated out and washed with cold alcohol. Yield 1.3 g (31%). M.p. 128-129° (from alcohol).

Found %: N 6.79, 6.95. $C_{10}H_{11}NS_2$. Calculated %: N 6.69.

Literature data for 3-o-tolylthiazolidinethione-2: m.p. 129° [6].

3-p-Anisylthiazolidinethione-2. From 3.66 g of N-(β-mercaptoethyl)-p-anisidine, 3.04 g of carbon bisulfide, and 1.12 g of potassium hydroxide was obtained 3.12 g (70%) of 3-p-anisylthiazolidinethione-2; m.p. 120.5-121° (from alcohol).

Found %: N 6.17, 5.89. $C_{10}H_{11}ONS_2$. Calculated %: N 6.27.

Literature data for 3-p-anisylthiazolidinethione-2: m.p. 120-121° [9].

3-o-Anisylthiazolidinethione-2. From 3.66 g of N-(β-mercaptoethyl)-o-anisidine, 3.04 g of carbon bisulfide, and 1.12 g of potassium hydroxide was obtained an oil that partially crystallized upon long standing. The crystals were separated out and washed with cold alcohol. Yield 0.25 g (5.5%). M. p.135.5-136°(from alcohol).

Found %: N 6.22, 6.40. $C_{10}H_{11}ONS_2$. Calculated %: N 6.27.

Literature data for 3-o-anisylthiazolidinethione-2: m.p. 136° [8].

3-Arylthiazolidones-2 from 3-Arylthiazolidinethiones-2

3-Phenylthiazolidone-2. A mixture of 0.5 g (0.0025 g-mole) of 3-phenylthiazolidinethione-2 and 1 g (0.0046 g-mole) of mercuric oxide in 10 ml of glacial acetic acid was boiled for 4 hours, whereupon in 5 minutes after the beginning of heating a precipitate of mercury sulfide started to separate out. Then the hot solution was filtered, the acetic acid was distilled off in vacuo, the crystalline residue was dissolved in hot, anhydrous methyl alcohol, and the solution was filtered from the insoluble inorganic contaminant. Upon cooling of the solution 0.31 g (70%) of crystals were obtained, which were 3-phenylthiazolidone-2; m.p. 76.5-77.5°. A mixed melting point test with known 3-phenylthiazolidone-2, prepared by us previously [3], showed no depression.

3-p-Tolylthiazolidone-2. A mixture of 0.5 g (0.0024 g-mole) of 3-p-tolylthiazolidinethione-2 and 1 g (0.0046 g-mole) of mercuric oxide in 10 ml of glacial acetic acid was boiled for 4 hours. After the reaction mass had been treated as described above, 0.28 g (60%) of 3-p-tolylthiazolidone-2 was obtained; m.p. 93-93.5° (from alcohol). A mixed melting point test with known 3-p-tolylthiazolidone-2 (m.p. 93-93.5°) prepared by us previously [3] showed no depression.

3-o-Tolylthiazolidone-2. A mixture of 0.21 g (0.001 g-mole) of 3-o-tolylthiazolidinethione-2 and 0.48 g

(0.022 g-mole) of mercuric oxide in 4 ml of glacial acetic acid was boiled for 4 hours. After appropriate treatment of the reaction mixture, 0.09 g (47%) of 3-o-tolylthiazolidone-2 was obtained; m.p. 61-62° (from alcohol). A mixed melting point test with known 3-o-tolylthiazolidone-2 (m.p. 61-62°) prepared by us previously [3] showed no depression.

3-p-Anisylthiazolidone-2. A mixture of 0.25 g (0.0011 g-mole) of 3-p-anisylthiazolidinethione-2 and 0.6 g (0.003 g-mole) of mercuric oxide in 5 ml of glacial acetic acid was boiled for 4 hours. After appropriate treatment of the reaction mass, 0.12 g (60%) of 3-p-anisylthiazolidone-2 was obtained; m.p. 102-103° (from alcohol). A mixed melting point test with known 3-p-anisylthiazolidone-2 (m.p. 102-103°) prepared by us previously [3] showed no depression.

3-o-Anisylthiazolidone-2. A mixture of 0.08 g (0.00035 g-mole) of 3-o-anisylthiazolidinethione-2 and 0.15 g (0.0007 g-mole) of mercuric oxide in 2 ml of glacial acetic acid was boiled for 4 hours. After appropriate treatment of the reaction mass as described above, 0.03 g (40%) of 3-o-anisylthiazolidone-2 was obtained; m.p. 116-117°. A mixed melting point test with known 3-o-anisylthiazolidone-2 prepared by us previously [3] showed no depression.

SUMMARY

Condensation of N-(β-mercaptoethyl)arylamines with carbon bisulfide in alcoholic medium in the presence of potassium hydroxide leads to the production of 3-arylthiazolidinethiones-2. In this way, in the present work, 3-phenyl-, 3-p-tolyl-, 3-o-tolyl-, 3-p-anisyl-, and 3-o-anisylthiazolidinethione-2 were prepared, which were converted by the action on them of mercuric oxide in glacial acetic acid to the corresponding 3-arylthiazolidones-2, by which means their structure was proved.

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CHEMISTRY OF SELENOPHENE

IX. CONDENSATION OF SELENOPHENE-2-CARBOXALDEHYDE WITH METHYL KETONES. SYNTHESIS AND REACTIONS OF 2-METHYLSELENOPHENE-5-CARBOXALDEHYDE

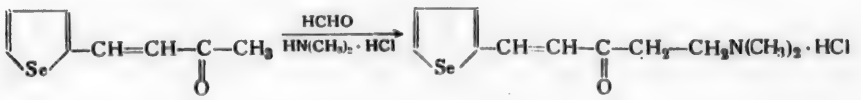
Yu. K. Yuryev, N. N. Mezentsova and V. E. Vaskovsky

In previous communications [1, 2] we had shown that selenophene-2-carboxaldehyde enters into many reactions characteristic of aromatic aldehydes, namely, the Cannizzaro and Perkin reactions, with ammonia, amines and with other compounds possessing labile hydrogen atoms, for example, with hippuric acid and rhodanine.

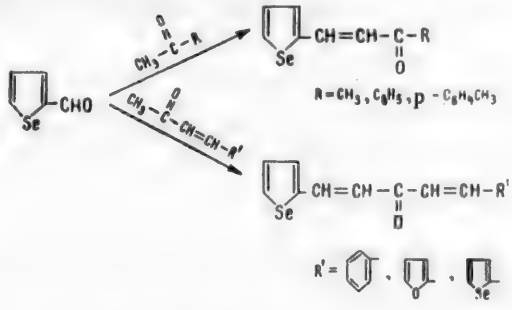
In the present study we continued our investigation of the reactivity of selenophene-2-carboxaldehyde on the examples of its condensation with methyl ketones. We also studied the reduction of selenophene-2-carboxaldehyde to 2-methylselenophene. We synthesized 2-methylselenophene-5-carboxaldehyde by the formylation of 2-methylselenophene, and prepared a number of its derivatives.

The reaction of selenophene-2-carboxaldehyde with aliphatic and aliphatic aromatic methyl ketones, namely, with acetone, acetophenone and methyl p-tolyl ketone, led to the formation of 2-selenenalacetone, α-(2-selenenal)acetophenone and α-(2-selenenal)-p-methylacetophenone, respectively.

The aminomethylation of 2-selenenalacetone by the Mannich reaction, employing the method described by one of us [3], gave 5-dimethylamino-1-(2-selenienyl)-1-penten-3-one hydrochloride.



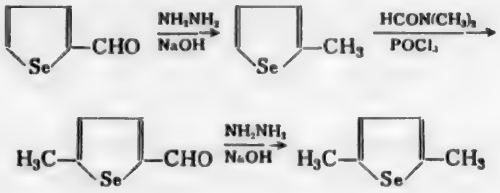
Selenophene-2-carboxaldehyde was also reacted with unsaturated methyl ketones, containing either the phenyl, furyl or selenienyl radical, and namely with benzalacetone, furfuralacetone and 2-selenenalacetone, which led to obtaining, respectively, 1-phenyl-5-(2-selenienyl)-1,4-pentadien-3-one, 1-furyl-5-(2-selenienyl)-1,4-pentadien-3-one and 1,5-di(2-selenienyl)-1,4-pentadien-3-one.



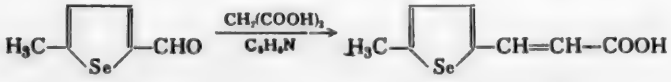
Since the N. M. Kizhner reaction has been successfully applied to aldehydes and ketones of the furan and thiophene series for the purpose of reducing their carbonyl groups to methyl and methylene groups, respectively,

we applied this reaction to selenophene-2-carboxaldehyde, and having decomposed its hydrazone with alkali, we obtained 2-methylselenophene in high yield (78.5%).

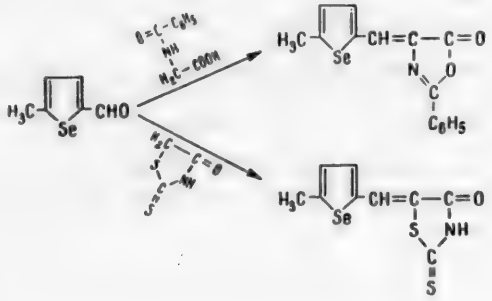
The formylation of 2-methylselenophene gave us 2-methylselenophene-5-carboxaldehyde in quantitative yield, and reduction of the aldehyde by the Kizhner method gave 2,5-dimethylselenophene in 87.5% yield.



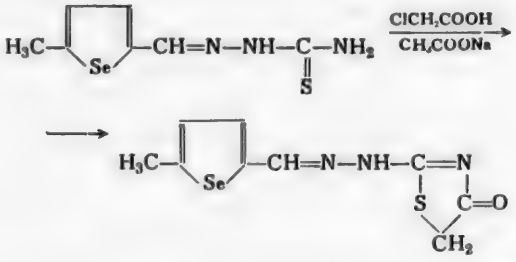
The condensation of 2-methylselenophene-5-carboxaldehyde with malonic acid gave us β-(2methylselenophen-5-yl)acrylic acid.



The reaction of 2-methylselenophene-5-carboxaldehyde with hippuric acid and with rhodanine gave respectively in quantitative yields 2-phenyl-4-(2-methyl-5-selenenal)-5-oxazolone and 5-(2-methyl-5-selenenal)-4--thiazolidone-2-thione.



The reaction of chloroacetic acid with 2-methylselenophene-5-carboxaldehyde in the presence of sodium acetate gave 2-methylselenophene-5-carboxaldehyde hydrazothiazolinone.



An attempt to introduce the formyl group in the β-position of the selenophene ring by the formylation of 2,5-dimethylselenophene proved unsuccessful: the 2,5-dimethylselenophene was recovered unchanged from the reaction.

EXPERIMENTAL

Condensation of Selenophene-2-carboxaldehyde With Methyl Ketones

2-Selenenalacetone. To a mixture of 11.0 g (0.068 mole) of selenophene-2-carboxaldehyde, 10.75 g (0.27 mole) of acetone and 7.6 ml of water was slowly added, with stirring, 2.5 ml of 10% sodium hydroxide solution at 18-20°. The reaction mixture was stirred for another 2.5 hours, then neutralized with 2N hydrochloric acid, and extracted with benzene. After distilling off the benzene the residue was vacuum-distilled twice. We obtained 10 g (71.5%) of 2-selenenalacetone:

B.p. 138-139° (5 mm); n_D^{20} 1.6578. d_4^{20} 1.4632, MR_D 50.09. $C_8H_8OSeF_3$. Calculated: 46.19.*

Found %: C 48.10, 48.13; H 4.22, 4.17. C_8H_8OSe. Calculated %: C 48.26; H 4.05.

5-Dimethylamino-1-(2-selenienyl)-1-penten-3-one Hydrochloride. Concentrated hydrochloric acid was added in drops to a mixture of 4.9 g (0.031 mole) of 2-selenenalacetone, 2.5 g (0.031 mole) of dimethylamine hydrochloride, 0.11 g of paraform and 0.5 ml of anhydrous alcohol. The mixture was heated on the water bath for 2 hours, cooled, and poured into 20 ml of acetone with ice cooling. We obtained 4 g (50%) of 5-dimethylamino--1-(2-selenienyl)-1-penten-3-one hydrochloride; white crystals with m.p. 165° (from a 5 : 1 mixture of alcohol and ether).

Found %: C 44.80, 44.85; H 5.71, 5.90; N 5.10, 5.29. $C_{11}H_{14}ONClSe$. Calculated %: C 45.15; H 5.5; N 4.78.

α-(2-Selenenal)acetophenone. Two ml of 20% sodium methylate solution was added to a mixture of 4.2 g (0.026 mole) of selenophene-2-carboxaldehyde and 3.4 g (0.026 mole) of acetophenone. The reaction mixture crystallized after standing for 48 hours at 0°. We obtained 3.4 g (50%) of α-(2-selenal)acetophenone; yellow crystals with m.p. 54° (from ligroin).

Found %: C 60.01. 60.18. H 4.01. 4.02. $C_{13}H_{10}OSe$. Calculated %: C 59.68; H 3.85.

α-(2-Selenenal)-p-methylacetophenone. To a mixture of 4 g (0.026 mole) of selenophene-2-carboxaldehyde and 3.6 g (0.026 mole) of methyl p-tolyl ketone was added 1.6 ml of 20% sodium methylate. On standing at 0° for 72 hours the reaction mixture crystallized. We obtained 3.6 g (52%) of α-(2-selenenal)-p-methylacetophenone; bright yellow crystals with m.p. 56° (from ligroin).

Found %: C 61.19, 61.13; H 4.35, 4.34. $C_{14}H_{12}OSe$. Calculated %: C 61.09; H 4.32.

1-Phenyl-5-(2-selenienyl)-1,4-pentadien-3-one. A solution of 3.7 g (0.025 mole) of freshly distilled benzalacetone in a mixture of 114 ml of alcohol, 160 ml of water and 20 ml of 10% sodium hydroxide solution was added to 4 g (0.025 mole) of selenophene-2-carboxaldehyde. We obtained 5 g (52.5%) of 1-phenyl-5-(2-selenienyl)-1,4-pentadien-3-one; dark yellow crystals with m.p. 96° (from 50% alcohol).

Found %: C 63.05, 62.94; H 4.31, 4.34. $C_{15}H_{12}OSe$. Calculated %: C 62.72; H 4.21.

1-Furyl-5-(2-selenienyl)-1,4-pentadien-3-one. A solution of 3.5 g (0.025 mole) of freshly distilled furfuralacetone in a mixture of 100 ml of alcohol, 160 ml of water and 20 ml of 10% sodium hydroxide solution was added to 4 g (0.025 mole) of selenophene-2-carboxaldehyde. We obtained 4.4 g (64%) of 1-furyl-5-(2-selenienyl)--1,4-pentadien-3-one as yellow crystals; m.p. 60° (from 50% alcohol).

Found %: C 56.04; 56.10; H 3.38, 3.49. $C_{13}H_{10}O_2Se$. Calculated %: C 56.32; H 3.63.

1,5-Di(2-selenienyl)-1,4-pentadien-3-one. A solution of 3.9 g (0.019 mole) of freshly distilled 2-selenenalacetone in a mixture of 70 ml of alcohol, 100 ml of water and 15 ml of 10% sodium hydroxide solution was added to 3 g (0.019 mole) of selenophene-2-carboxaldehyde. The reaction mixture was allowed to stand for 24 hours at 0°. We obtained 3.35 g (52%) of 1,5-di(2-selenienyl)-1,4-pentadien-3-one as yellow crystals; m.p. 128° (from 50% alcohol).

Found %: C 46.11, 46.15; H 3.00, 2.96. $C_{13}H_{10}OSe_2$. Calculated %: C 45.80; H 2.96.

2-Methylselenophene-5-carboxaldehyde and Its Reactions

2-Methylselenophene. To a solution of 35 g (0.218 mole) of selenophene-2-carboxaldehyde and 45 ml of

*The molecular refraction was calculated with the atomic refraction of selenium taken equal to 10.64.

80% hydrazine hydrate in 200 ml of diethylene glycol, contained in a flask under reflux, was added 27 g of crushed sodium hydroxide. The mixture was first heated in an oil bath at 120-130° (15-20 minutes), and then (after the stormy evolution of nitrogen had ceased) at 170-180° (30-40 minutes). Then the fraction with b.p. up to 140° was distilled off, which was washed with 10% hydrochloric acid, then with water, dried over calcium chloride, and distilled, in which connection the main portion distilled at 134-136°. After 2 distillations of this fraction over sodium we obtained 25.1 g (78.5%) of 2-methylselenophene:

B.p. 136-136.2° (769 mm); n_{20}^{D} 1.5615; d_4^{20} 1.4432, MR_D 32.57. $C_5H_6SeF_2$. Calculated: 32.79.

Found %: C 41.88, 41.72; H 4.46, 4.31. C_5H_6Se. Calculated %: C 41.39; H 4.17.

Literature for 2-methylselenophene: b.p. 131-132°; n_D^{20} 1.5534, d_4^{20} 1.4242 [4].

2-Methylselenophene-5-carboxaldehyde. To 14.6 g (0.2 mole) of dimethylformamide, contained in a three-necked flask, fitted with dropping funnel, reflux condenser and stirrer, was added 31 g (0.2 mole) of phosphorus oxychloride in 5-6 minutes and a temperature of 5°. The reaction mixture was allowed to stand for 15 minutes at 20°, after which 50 ml of dichloroethane was added, and to the obtained solution at 5° was slowly added with stirring a solution of 25 g (0.17 mole) of 2-methylselenophene in 30 ml of dichloroethane.

Then the mixture was refluxed for 15 minutes, cooled, and poured into a solution of 130 g of sodium acetate in 175 ml of water; the solution was heated nearly to the boil and then cooled. The dichloroethane and ether extracts were dried over anhydrous sodium sulfate. After distilling off the ether and dichloroethane the residue was vacuum-distilled in a stream of nitrogen, in which connection the fraction distilling at 103-105° (9 mm) was collected. After redistillation in vacuo we obtained 26.1 g (87.5%) of 2-methylselenophene-5-carboxaldehyde:

B.p. 96-97° (7 mm), n_D^{20} 1.6160, d_4^{20} 1.5427, MR_D 39.20. $C_6H_6OSeF_2$. Calculated: 37.42.

Found %: C 41.67, 41.53; H 3.51, 3.48. C_6H_6OSe. Calculated %: C 41.67; H 3.48.

2-Methylselenophene-5-carboxaldehyde Semicarbazone. We obtained 1.1 g of the semicarbazone from 1 g of the aldehyde (in 5 ml of alcohol), 1 g of semicarbazide hydrochloride and 1.6 g of sodium acetate: its m.p. 209° (from 90% alcohol).

Found %: N 18.34, 18.56. $C_7H_9ON_3Se$. Calculated %: N 18.21.

2-Methylselenophene-5-carboxaldehyde 2,4-Dinitrophenylhydrazone. We obtained 0.9 g of the hydrazone from 0.5 g of the aldehyde (in 20 ml of alcohol), 0.4 g of 2,4-dinitrophenylhydrazine (in 1.5 ml of concentrated sulfuric acid and 2 ml of water) and 8 ml of alcohol: its m.p. 241° (from pyridine).

Found %: N 15.16, 15.03. $C_{12}H_{10}O_4N_4Se$. Calculated %: N 15.58.

2-Methylselenophene-5-carboxaldehyde Thiosemicarbazone. We obtained 6.4 g of the thiosemicarbazone from 5 g of the aldehyde (in 50 ml of 50% alcohol), 1.65 ml of glacial acetic acid and 2.8 g of thiosemicarbazide hydrochloride: its m.p. 149° (from alcohol).

Found %: N 16.94, 16.74. $C_7H_9N_3SSe$. Calculated %: N 17.06.

2-Methylselenophene-5-carboxaldehyde Hydrazothiazolinone. To a solution of 3.4 g (0.015 mole) of 2-methylselenophene-5-carboxaldehyde in 80 ml of alcohol were added 3.5 g of anhydrous sodium acetate and 3.5 g of chloroacetic acid; the mixture was heated for 1 hour on the water bath. The obtained precipitate was washed with hot water and alcohol. We obtained 3.4 g (81%) of 2-methylselenophene-5-carboxaldehyde hydrazothiazolinone: light yellow crystals with m.p. 255°.

Found %: C 38.01, 38.18; H 3.30. 3.46; N 14.81, 15.02. $C_9H_9ON_3SSe$. Calculated %: C 37.76; H 3.16; N 14.67.

5-(2-Methyl-5-selenenal)-4-thiazolidone-2-thione. To a slightly warm solution of 3 g (0.019 mole) of 2-methylselenophene-5-carboxaldehyde and 2.5 g (0.019 mole) of rhodanine in 17.5 ml of glacial acetic acid was added 4.65 g of anhydrous sodium acetate. The mixture was heated for 30 minutes and then treated with 100 ml of water; the precipitate was separated, and washed with water, alcohol and ether. We obtained 3.95 g (80%) of 5-(2-methyl-5-selenenal)-4-thiazolidone-2-thione: lustrous brown crystals with m.p. 236°.

Found %: C 37.69; 37.54; H 2.67, 2.51; N 5.22, 5.13. $C_9H_7ONS_2Se$. Calculated %: C 37.49; H 2.44; N 4.86.

Phenyl -4-(2-methyl-5-selenenal)-5-oxazolone. A mixture of 2 g (0.012 mole) of 2-methylselenophene-5-carboxaldehyde, 2.34 (0.012 mole) of hippuric acid, 0.97 g of anhydrous sodium acetate and 10 ml of acetic anhydride was heated for 1 hour on the water bath at 60-70°. We obtained 2.9 g (83%) of 2-phenyl-4-(2-methyl-5-selenenal)-5-oxazolone; bright yellow crystals with m.p. 156° (from benzene).

Found %: C 56.91, 56.95; H 3.90, 3.88; N 4.75, 4.82. $C_{15}H_{11}O_2NSe$. Calculated %: C 56.95; H 3.50; N 4.43.

β-(2-Methylselenophen-5-yl)acrylic Acid. A mixture of 3 g (0.017 mole) of 2-methylselenophene-5-carboxaldehyde, 1.81 g (0.017 mole) of malonic acid and 1.75 ml of dry pyridine was heated for 4 hours on the water bath, after which 29 ml of saturated soda solution was added. The unchanged aldehyde and pyridine were steam-distilled. The residue was acidified with hydrochloric acid. We obtained 2.2 g (60%) of β-(2-methylselenophen-5-yl)acrylic acid; light yellow crystals with m.p. 162° (from water).

Found %: C 44.70, 44.94; H 4.01, 3.89. $C_8H_8O_2Se$. Calculated %: C 44.66; H 3.74.

2,5-Dimethylselenophene. The procedure described above was used to reduce 2-methylselenophene-5-carboxaldehyde to 2,5-dimethylselenophene. From 26 g (0.15 mole) of 2-methylselenophene-5-carboxaldehyde, 30 ml of 80% hydrazine hydrate, 18 g of sodium hydroxide and 150 ml of diethylene glycol we obtained 20.9 g (87.5%) of 2,5-dimethylselenophene:

B.p. 154-154.5° (755 mm); n_D^{20} 1.5504, d_4^{20} 1.3697, MR_D 37.00. C_6H_8Se. Calculated MR_D 37.41.

Found %: C 45.50, 45.41; H 5.14, 5.21. C_6H_8Se. Calculated %: C 45.29, H 5.07.

Literature for 2,5-dimethylselenophene: b.p. 154-156°, n_D^{20} 1.5438, d_4^{20} 1.3434 [4].

SUMMARY

1. The condensations of selenophene-2-carboxaldehyde with methyl ketones proceed smoothly and lead to the formation of unsaturated ketones, containing the selenophene ring. In this manner we obtained 2-selenenalacetone, α-(2-selenenal)acetophenone, α-(2-selenenal)-p-methylacetophenone, 1-phenyl-5-(2-selenienyl)-1,4-pentadien-3-one, 1-furyl-5-(2-selenienyl)-1,4-pentadien-3-one and 1,5-di(2-selenienyl)-1,4-pentadien-3-one.

2. The aminomethylation of 2-selenenalacetone by the Mannich reaction leads to the formation of 5-dimethylamino-1-(2-selenienyl)-1-penten-3-one hydrochloride.

3. The reduction of selenophene-2-carboxaldehyde and 2-methylselenophene-5-carboxaldehyde (obtained by the formylation of 2-methylselenophene) by the Kizhner reaction leads to the formation of 2-methylselenophene and 2,5-dimethylselenophene, respectively.

4. The condensation of 2-methylselenophene-5-carboxaldehyde with hippuric acid, rhodanine and with malonic acid leads to the formation of 2-phenyl-4-(2-methyl-5-selenenal)-5-oxazolone, 5-(2-methyl-5-selenenal)-4-thiazolidone-2-thione and β-(2-methylselenophen-5-yl)acrylic acid, respectively.

5. The condensation of 2-methylselenophene-5-carboxaldehyde thiosemicarbazone with chloroacetic acid leads to the formation of 2-methylselenophene-5-carboxaldehyde hydrazothiazolinone.

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*Original Russian pagination. See C. B. translation.

ALKALOIDS OF PIPTANTHUS NANUS

ISOLATION OF ISOPIPTANTHINE

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Two new alkaloids – piptanthine and piptamine – were isolated by Konovalova and Diskina in 1951 from the Central Asian plant Piptanthus nanus [1].

In the present communication we describe the isolation of still another new base from this plant, which has the composition $C_{14}H_{24}N_2$ and is isomeric with the above-mentioned alkaloids, as a result of which we have proposed to call it isopiptanthine. This base is optically inactive and in its properties lies very close to piptanthine and piptamine [2]. Similar to these two alkaloids, isopiptanthine has one secondary nitrogen atom, which when methylated with methyl iodide gave N-methylisopiptanthine having the composition $C_{15}H_{26}N_2$.

Reaction of isopiptanthine with formaldehyde in formic acid, similar to the situation with piptanthine and piptamine [3], yields the condensation product of isopiptanthine with formaldehyde ($C_{15}H_{24}N_2$), which no longer has a secondary nitrogen atom, but at the same time it does not contain a methylimido group and is not identical with the product obtained by the methylation of isopiptanthine with methyl iodide.

Apparently, the condensation of isopiptanthine with formaldehyde proceeds with the closure of a new ring and the formation of a sparteine skeleton; consequently it may be assumed that isopiptanthine is a stereoisomer of the two alkaloids isolated earlier from Piptanthus nanus.

EXPERIMENTAL

The plant raw material (15 kg of the above ground portions of Piptanthus nanus) was extracted in essentially the same manner as described by Konovalova and Diskina for the isolation of the alkaloids piptanthine and piptamine.

Isolation of Isopiptanthine. The free bases, extracted with ether from the weakly alkaline solution (the acid extract was made alkaline with sodium bicarbonate) and containing piptanthine with a small amount of isopiptanthine, were treated with hot alcohol. The insoluble precipitate of isopiptanthine (0.87 g) was recrystallized 3 times from alcohol, after which it had m.p. 216-218°. The yield of isopiptanthine was 0.006%.

Found %: C 76.51, 76.45; H 10.83, 10.99; N 12.93, 13.02. $C_{14}H_{24}N_2$. Calculated %: C 76.37; H 10.90; N 12.72.

Isopiptanthine Nitrate was obtained as a crystalline precipitate when the free base was treated with 10% nitric acid solution. After recrystallization from water, m.p. 221-223°. The nitrate, after drying, readily absorbs moisture from the air to again form the salt with water of crystallization.

Found %: C 46.45; H 8.00; N 15.67; H_2O 4.62. $C_{14}H_{24}N_2 \cdot 2HNO_3 \cdot H_2O$. Calculated %: C 46.15; H 7.69; N 15.39; H_2O 4.94.

Isopiptanthine Hydriodide was obtained as a crystalline precipitate when a hydrochloric acid solution of isopiptanthine was treated with a water solution of KI. M.p. 304-306°.

Isopiptanthine Picrate was obtained by mixing an alcohol solution of the free base with an alcohol solution of picric acid. M.p. 162-165°.

Methylation of Isopiptanthine With Methyl Iodide. A solution of 0.2 g of isopiptanthine with m.p. 216-218° in 6 ml of methyl alcohol was heated with 0.5 ml of methyl iodide on the water bath for 5 hours. After removal of the solvent the crystalline N-methylisopiptanthine hydriodide was washed with acetone and recrystallized from alcohol. M.p. 249-252°.

N-Methylisopiptanthine was isolated from the hydriodide by precipitation with ammonia and extraction with ether. After removal of the ether the free base was recrystallized from acetone. M.p. 116-118°.

Found %: C 76.78; H 11.03; N 12.28. $C_{15}H_{26}N_2$. Calculated %: C 76.92; H 11.11; N 11.96.

Condensation of Isopiptanthine With Formaldehyde. A solution of 0.3 g of isopiptanthine (free base) with m.p. 216-218° in 0.5 ml of 28% formic acid was heated for 5 hours on the water bath with 0.3 ml of 35% formaldehyde solution. The cooled solution was diluted with 3 ml of water, and then excess 25% ammonia was added. This gave a water-insoluble free base as precipitate (0.45 g), which was recrystallized from acetone. M.p. 166--168°.

Found %: C 77.31; H 10.23; N 12.38. $C_{15}H_{24}N_2$. Calculated %: C 77.59; H 10.35; N 12.07. Devoid of the NCH_3 group.

SUMMARY

1. A new optically inactive free base ($C_{14}H_{24}N_2$) was isolated from Piptanthus nanus, which is isomeric with piptanthine, has m.p. 216-218°, and has been named isopiptanthine.

2. Isopiptanthine contains a secondary nitrogen atom and when methylated with methyl iodide gives N--methylisopiptanthine ($C_{15}H_{26}N_2$) with m.p. 112-116°.*

3. The condensation of isopiptanthine with formaldehyde gave a condensation product ($C_{15}H_{24}N_2$) with m.p. 166-168°.

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* As in original. Possibly 116-118° is correct. Publisher's note.
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SYNTHESIS OF ALKALOID ARECOLINE AND ITS HOMOLOGS

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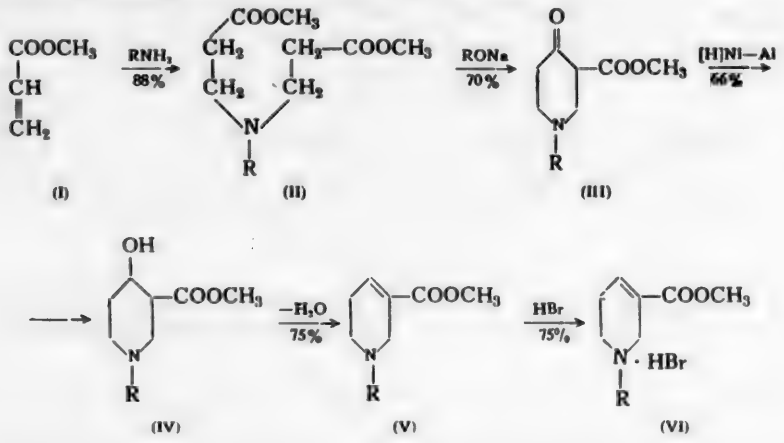
Arecoline — an alkaloid found in the fruit of the palm Areca Catechu [1] — has found extensive use in veterinary practice as an anthelmintic and as a compound for increasing intestinal peristalsis. It was established by investigations [2] that in chemical structure arecoline is the methyl ester of N-methyl-1,2,5,6-tetrahydronicotinic acid (VI, R = CH_3). The synthesis of arecoline has been accomplished by several methods: from nicotinic acid [3], from citric acid [4], from β-halo derivatives of propionic ester [5], and from the nitrile or esters of acrylic acid [6].

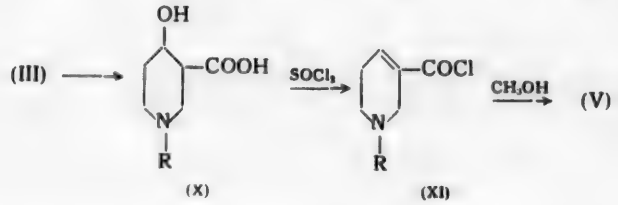
We investigated the most practical method for the preparation of arecoline and its homologs with various substituents on the nitrogen, proceeding from methyl acrylate (I) by the scheme



(I) (II) (III) (IV) (V) (VI)

The reaction of methyl acrylate (I) with alkylamines leads to the formation of β,β'-dicarbomethoxydiethylalkylamines (II). Closure of (II) with the formation of the N-alkyl-3-carbomethoxy-4-piperidone (III) was accomplished by heating diester (II) with sodium or with alcoholates. Care must be taken when sodium is used to effect cyclization of the diester, since the reaction usually begins suddenly and is exothermic. It is preferable to run this stage of the synthesis in the presence of sodium methylate. The next step in the synthesis of arecoline and its homologs is the reduction of the N-alkyl-3-carbomethoxy-4-piperidone (III) to the N-alkyl-3-carbomethoxy-4-hydroxypiperidine (IV). This was accomplished by several methods. Catalytic reduction in the presence of platinum oxide requires the purification of ketone (III) by recrystallization of its hydrochloride from alcohol. The electrochemical reduction of ketone (III) in alkaline medium results in the simultaneous saponification of the ester group. The N-alkyl-4-hydroxypiperidine-3-carboxylic acid (X) formed here can be esterified in the usual manner to give the methyl ester (IV). The most convenient method is to run the reduction in the presence of skeletal nickel catalyst. The reduction is run at 30-60 atm and a temperature not exceeding 50°; this method, the same as the electrochemical method, does not require special purification of the ketone. The hydrogenation product is the N-alkyl-3-carbomethoxy-4-hydroxypiperidine (IV). The dehydration of (IV) is accomplished by

the use of phosphorus trichloride, phosphorus oxychloride, hydrobromic acid, and other water-removing substances. The best results were obtained with thionyl chloride. It should be mentioned that when the electrochemical method is used to reduce ketone (III) it is wiser to first dehydrate the N-alkyl-4-hydroxypiperidine-3-carboxylic acid (X), and then react the formed acid chloride (XI) with methyl alcohol to convert it to the methyl ester of the N--alkyl-Δ^3-tetrahydronicotinic acid (V). All of the obtained methyl esters (V) are liquids and possess basic properties.



The hydrobromides of the methyl esters, obtained by the reaction of an alcohol solution of hydrogen bromide or of hydrobromic acid with either an ether or benzene solution of the free base, were subjected to physiological testing.

The N-substituted derivatives of β,β'-dicarbomethoxydiethylamine (II) were also obtained by other methods.

$$HN(CH_2CH_2CN)_2 \leftarrow CH_2{=}CH{-}CN \rightarrow RN(CH_2CH_2CN)_2 \rightarrow (II)$$
(VIII) (VII) (IX)

β,β'-Dicyanodiethylamine (VIII) was prepared from acrylonitrile (VII) and ammonia. Alkylation of (VIII) with alkyl halides or with aldehydes and formic acid gave the β,β'-dicyanodiethylalkylamines (IX). The N-substituted β,β'-dicyanodiethylamines (IX) are also formed by the direct reaction of acrylonitrile (VII) with the corresponding alkylamines. The heating of the β,β'-dicyanodiethylalkylamines (IX) with methyl alcohol in the presence of either hydrogen chloride or sulfuric acid gave the β,β'-dicarbomethoxydiethylalkylamines (II).

EXPERIMENTAL

1. β,β'-Dicyanodiethylamine (VIII). To 145 ml of 26% ammonia solution was gradually added with stirring 200 g of acrylonitrile (VII) at 25-28°. The reaction mass was stirred until the separate layers disappeared (about 3 hours), after which the water was removed by vacuum-distillation, and then the residue was distilled. We obtained two fractions – monocyanoethylamine and β,β'-dicyanodiethylamine (VIII). It should be mentioned that the best yield in the reaction of acrylonitrile with ammonia is obtained when the ammonia concentration is not less than 26% and the mole ratio of the reactants is 1 : 0.53 [7]. If this ratio is increased the amount of mono derivative increases [8], which can be converted into β,β'-dicyanodiethylamine by condensation with the calculated amount of acrylonitrile. Yield of β-cyanoethylamine 5.1 g. B.p. 76-78° at 9 mm. Yield of β,β'-dicyanodiethylamine 205 g (88.3%).

B.p. 184-186° at 9 mm, d_4^{20} 1.0194, n_D^{20} 1.4645, MR_D 33.42; calc. 33.05.

Found %: C 58.58; H 7.59; N 34.21. $C_6H_9N_3$. Calculated %: C 58.52; H 7.36; N 34.12.

β,β'-Dicyanodiethylmethylamine (IX, R = CH_3). a) Methylation With Formalin and Formic Acid. To 100 g of β,β'-dicyanodiethylamine (VIII) was added gradually, with stirring and external cooling with water, a mixture of 50 g of 83% formic acid and 160 ml of 40% formalin at such a rate that the temperature did not exceed 25°. Then the reaction mass was heated gradually to 70-75° and kept at this temperature for 2 hours. A copious evolution of carbon dioxide was observed at 40-50°. On conclusion of reaction the mass was cooled to 10° and a saturated potash solution was added until alkaline to phenolphthalein. Dinitrile (IX) was extracted from the solution with chloroform. The solvent was distilled off, and the residue was distilled. Yield of (IX) 92.5 g (83%).

B.p. 178-180° at 12 mm, 148-150° at 3 mm.

Found %: C 61.26; H 8.31; N 30.56. $C_7H_{11}N_3$. Calculated %: C 61.31; H 8.08; N 30.77.

b) Reaction of Methylamine With Acrylonitrile. A mixture of 55.8 g of 95% calcined soda in 130 ml of

water, 111 g of acrylonitrile (VII) and 67.5 g of methylamine hydrochloride was stirred for 1 hour, in which connection the temperature rose to 40-45°. The reaction mass was heated gradually to 100° (about 1 hour), the reflux condenser replaced by a descending condenser, and the mixture of unreacted acrylonitrile and water distilled off. The residue was cooled to 18-20°, the upper layer of β,β'-dicyanodiethylmethylamine was separated, and the bottom aqueous layer was extracted 3 times with 50 ml portions of benzene. The benzene extracts were added to the main layer, the solvent distilled off, and the residue was distilled. Yield of (IX) 122 g (85.1%).

B.p. 166-167° at 8 mm, d_4^{20} 0.9900, n_D^{20} 1.4618, MR_D 38.03. $C_7H_{11}N_3$. Calculated MR_D 38.01.

c) Alkylation of β,β'-Dicyanodiethylamine (VIII) With Alkyl Halides. β,β'-Dicyanodiethylamine (IX, R = C_2H_5). To a solution of 15 g of β,β'-dicyanodiethylamine (VIII) in 25 ml of anhydrous ethyl alcohol was added 19 g of ethyl iodide and 10 g of a sodium bicarbonate. The mixture was refluxed with stirring for 6 hours. The alcohol was removed by vacuum-distillation, 50 ml of water was added to the residue, and the compound was extracted with chloroform (3 times with 20 ml portions). After distilling off the solvent the residue was distilled. Yield of β,β'-dicyanodiethylethylamine 16 g (86.8%).

B.p. 177-178° at 10 mm, d_4^{20} 0.9730, n_D^{20} 1.4617, MR_D 42.64; calc. 42.62.

Found %: C 63.49; H 8.67; N 27.81. $C_8H_{13}N_3$. Calculated %: C 63.40; H 8.66; N 27.78.

The homologs of β,β'-dicyanodiethylamine: n-propyl (IX, R = n-C_3H_7), n-butyl (IX, R = n-C_4H_9) and benzyl (IX, R = $CH_2C_6H_5$) were obtained in a similar manner.

(IX, R = n-C_3H_7). Yield 85.5%. B.p. 176-177° at 9 mm, d_4^{20} 0.9620, n_D^{20} 1.4610, MR_D 47.10; calc. 47.24.

Found %: C 65.49; H 8.99; N 25.67. $C_9H_{15}N_3$. Calculated %: C 65.42; H 9.09; N 25.43.

(IX, R = n-C_4H_9). Yield 77.5%. B.p. 179-180° at 9 mm, d_4^{20} 0.9501, n_D^{20} 1.4610, MR_D 51.85; calc. 51.86.

Found %: C 67.26; H 9.25; N 23.59. $C_{10}H_{17}N_3$. Calculated %: C 66.99; H 9.56; N 23.44.

(IX, R = $CH_2C_6H_5$). Yield 83.6%. B.p. 248-249° at 13 mm, d_4^{20} 1.0697, n_D^{20} 1.5285, MR_D 61.44; calc. 62.11.

Found %: C 73.28; H 7.22; N 19.53. $C_{13}H_{15}N_3$. Calculated %: C 73.26; H 7.09; N 19.70.

2. β,β'-Dicarbomethoxydiethylmethylamine (II, R = CH_3). a) Esterification of β,β'-Dicyanodiethylmethylamine (IX) With Methyl alcohol in the presence of sulfuric acid. To a solution of 30 g of β,β'-dicyanodiethylmethylamine (IX) in 132 ml of methyl alcohol was gradually added with stirring 66 g of concentrated sulfuric acid. Then the mixture was boiled in an oil bath for 20 hours, gradually raising the temperature of the bath to 120-125°, after which the excess alcohol was removed by vacuum-distillation. The residue after cooling was was treated with 60 ml of water and a saturated solution of potash until it showed alkaline to phenolphthalein. The deposit of mineral salts was filtered and washed with chloroform (3 times with 50 ml portions). The wash chloroform was used to extract the diester from the filtrate, after which the solvent was distilled off, and the residue was vacuum-distilled. Yield of β,β'-dicarbomethoxydiethylmethylamine (II) 33.1 g (74.5%).

B.p. 135-136° at 12 mm, d_4^{20} 1.0620, n_D^{20} 1.4451, MR_D 50.94; calc. 51.01.

Found %: C 53.25; H 8.32; N 6.92. $C_9H_{17}O_4N$. Calculated %: C 53.20; H 8.43; N 6.89.

b) Esterification With Methyl Alcohol in the Presence of Hydrogen Chloride. To 67 g of β,β'-dicyanodiethylmethylamine (IX) was gradually added with stirring 300 ml of methyl alcohol, previously saturated with 108 g of hydrogen chloride, at such a rate that the temperature remained at 48-55°. After all of the methyl alcohol had been added the reaction mass was heated at 67-70° for 3 hours. After cooling, the precipitate of ammonium chloride was filtered and washed with methyl alcohol (twice with 30 ml portions). The alcohol was distilled from the filtrate, and the residue under good cooling was neutralized with a saturated solution of potash (to phenolphthalein). The obtained precipitate was filtered and washed with chloroform (3 times with 50 ml portions). The diester was extracted from the mother liquor with chloroform. After removal of the solvent the residue was vacuum-distilled. Yield of β,β'-dicarbomethoxydiethylmethylamine (II) 84.5 g (85.1%). B.p. 130-131° at 11 mm.

c) Condensation of Methyl Acrylate With Methylamine Hydrochloride was accomplished by the same method used to prepare β,β'-dicyanodiethylmethylamine.

d) Reaction of Methyl Acrylate (I) With Methylamine. A solution of 6 g of methylamine in 50 ml of methyl alcohol was gradually added with stirring, at 5-10°, to 34.5 g of freshly distilled methyl acrylate (I) (b.p. 78-80°). After all of the methyl alcohol solution had been added the reaction mass was allowed to stand at room temperature for 20 hours, then it was heated at the boil for 3 hours, after which the methyl alcohol was distilled off, and the residue was distilled. Yield of β,β'-dicarbomethoxydiethylmethylamine (II) 35.9 g (88.2%). B.p. 127-128° at 10 mm.

The homologs of β,β'-dicarbomethoxydiethylmethylamine: ethyl (II, R = C_2H_5), n-propyl (II, R = n-C_3H_7), n-butyl (II, R = n-C_4H_9) and benzyl (II, R = $CH_2C_6H_5$) were obtained by a similar procedure.

(II, R = C_2H_5). Yield 66.5%. B.p. 124° at 8 mm, d_4^{20} 1.0394, n_D^{20} 1.4450, MR_D 55.63; calc. 55.65.

Found %: C 55.45; H 8.86; N 6.51. $C_{10}H_{19}O_4N$. Calculated %: C 55.26; H 8.81; N 6.44.

(II, R = n-C_3H_7). Yield 63.3%. B.p. 135° at 9 mm, d_4^{20} 1.0185, n_D^{20} 1.4459, MR_D 60.54; calc. 60.24.

Found %: C 57.21; H 9.26; N 6.02. $C_{11}H_{21}O_4N$. Calculated %: C 57.11; H 9.15; N 6.05.

(II, R = n-C_4H_9). Yield 48.4%. B.p. 145° at 9 mm, d_4^{20} 1.0032, n_D^{20} 1.4465, MR_D 65.27; calc. 64.86.

Found %: C 58.84; H 9.62; N 5.78. $C_{12}H_{23}O_4N$. Calculated %: C 58.75; H 9.45; N 5.71.

3. N-Methyl-3-carbomethoxy-4-piperidone (III, R = CH_3). To a suspension of 23.7 g of pulverized sodium methylate in 120 ml of dry benzene was added with stirring 81.2 g of β,β'-dicarbomethoxydiethylmethylamine (II), in which connection the temperature rose to 40-50°. The reaction mass was heated for 3 hours, then cooled to 10°, and finally treated with 220 ml of water. The mixture was stirred until the sodio derivative of the ketone had all dissolved, after which the benzene layer was separated, while the water layer was neutralized with the calculated amount of either glacial acetic acid or concentrated hydrochloric acid, followed by the addition of saturated potash solution (to phenolphthalein), and finally the ketone was extracted with benzene (8 times with 50 ml portions). The solvent was removed by vacuum-distillation. The residue, representing technical N-methyl--3-carbomethoxy-4-piperidone, was used as such for its catalytic reduction in the presence of Raney nickel catalyst or by the electrochemical method. Yield 48.2 g (70.4%).

The homologs of N-methyl-3-carbomethoxy-4-piperidone: ethyl (III, R = C_2H_5), n-propyl (III, R = n-C_3H_7), (III, R = n-C_4H_9) and benzyl (III, R = $CH_2C_6H_5$) were prepared by a similar procedure. All of the bases are liquids, readily soluble in water and organic solvents, and give a characteristic violet color with ferric chloride. For their physicochemical characterization the free bases were converted to either their hydrochloride or hydrobromide by treating an ether solution of the ketone base (1 : 3) with an alcohol solution of either hydrogen chloride or hydrogen bromide. After two recrystallizations from anhydrous ethyl alcohol the salts were obtained pure.

(III, R = CH_3 · HCl). Yield 85%. B.p. 166-168°.

Found %: C 46.69; H 6.71; N 7.00. $C_8H_{13}O_3N$ · HCl. Calculated %: C 46.27; H 6.79; N 6.74.

(III, R = C_2H_5 · HCl). Yield 92%. B.p. 150-152°.

Found %: C 48.69; H 7.00; N 6.31. $C_9H_{15}O_3N$ · HCl. Calculated %: C 48.75; H 7.27; N 6.32.

(III, R = n-C_3H_7 · HCl). Yield 78%. B.p. 158-160°.

Found %: N 5.83. $C_{10}H_{17}O_3N$ · HCl. Calculated %: N 5.94.

(III, R = n-C_4H_9 · HCl) Yield 80%. B.p. 136-140°.

Found %: N 5.66. $C_{11}H_{19}O_3N$ · HCl. Calculated %: N 5.60.

(III, R = $CH_2C_6H_5$ · HNO_3). B.p. 132-134°.

Found %: N 8.87. $C_{14}H_{17}O_3N$ · HNO_3. Calculated %: N 9.03.

(III, R = $CH_2C_6H_5$ · HBr). B.p. 165-167°.

Found %: N 4.44. $C_{14}H_{17}O_3N$ · HBr. Calculated %: N 4.27.

4. N-Methyl-3-carbomethoxy-4-hydroxypiperidine (IV, R = CH_3). a) Reduction in the Presence of Platinum Oxide. Into an autoclave was charged 11 g of N-methyl-3-carbomethoxy-4-piperidone hydrochloride (III, R = CH_3 · HCl),

50 ml of methyl alcohol and 0.5 g of platinum oxide. The hydrogenation was run at an initial hydrogen pressure of 100 atm and a temperature of 100° for 5 hours. On conclusion of reduction (absence of a color with ferric chloride) the reaction mass was filtered from the catalyst, and the alcohol was removed by distillation. The residue was dissolved in 40 ml of water and with cooling was treated with a saturated solution of potash (to phenolphthalein). The piperidols were extracted from the solution with chloroform. The solvent was distilled off, and the residue was distilled. The mixed N-methyl-3-carbomethoxy-4-hydroxypiperidines (IV) were obtained as a viscous oil that graducally crystallized. Yield 6.5 g (70.9%). B.p. 112-118° at 5 mm.

b) Reduction in the Presence of Raney Nickel Catalyst. Into a rotating stainless steel autoclave was charged 48.2 g of freshly prepared technical ketone (III, R = CH_3) and a suspension of 8.6 g of Raney nickel catalyst in 20 ml of anhydrous methyl alcohol. The reduction was run at an initial hydrogen pressure of 30-50 atm and a temperature of 45-50° for 3-4 hours. Then, after cooling the methanol solution, the piperidols were filtered from the catalyst. The alcohol was distilled off, and the residue was distilled. The mixed N-methyl--3-carbomethoxy-4-hydroxypiperidines (IV) were obtained as a crystalline mass. Yield 32.1 g (65.9%). B.p. 130-135° at 20 mm. Recrystallization of the obtained mixture of piperidols from 2 parts of ethyl alcohol gave the piperidol as lustrous white crystals. M.p. 86-87°.

Found %: C 55.49; H 8.70; N 8.08. $C_8H_{15}O_3N$. Calculated %: C 55.49; H 8.73; N 8.09.

c) Electrochemical Reduction at Lead Electrodes in Alkaline Medium. A mixture of 470 ml of 1.15 N potassium hydroxide solution and 25 g of N-methyl-3-carbomethoxy-4-piperidone (III, R = $CH_3 \cdot HCl$) was charged into a 600 ml porous dish. Then a lead cathode (1.795 sq dm) was inserted and a U-shaped tube for cooling the reaction mass with a stream of water. A lead anode (3.31 sq dm) was placed in the space between the porous dish and a 1.5 liter porcelain beaker and the whole was filled with 10% calcined soda solution. The reduction was run with a current strength of 8 amp and a difference in the potentials of 6 v for 8-9 hours at a temperature of 20-22°. The end of reduction was established by the failure to obtain a violet color with ferric chloride. Then the reaction mass was acidified with hydrochloric acid (to congo) and the solution was evaporated in vacuo. The hydrochlorides of the N-methyl-4-hydroxyhexahydronicotinic acids were extracted from the dry residue with hot methyl alcohol. Removal of the solvent by vacuum-distillation gave the hydrochlorides of the technical acids (X, R = CH_3), which without further purification were subjected to dehydration. Yield 21.7 g (91.9%).

5. Methyl N-Methyl-Δ^3-tetrahydronicotinate, Arecoline Base (V, R = CH_3). a) From the hydroxy derivative (IV, R = CH_3). To 6 g of thionyl chloride with external cooling in ice water and stirring was added a solution of 10.4 g of N-methyl-3-carbomethoxy-4-hydroxypiperidine (IV) in 10 ml of methylene chloride; the rate of adding the piperidol was regulated so that the temperature did not rise above 50°. Then the reaction mass was heated at the boil for 2 hours, after which the solvent and excess thionyl chloride were distilled off. The residue after cooling was treated with 10 ml of methanol and the whole allowed to stand at room temperature for 2 hours. Then the mass was heated at the boil for 1 hour and the alcohol was removed by vacuum-distillation. The residue was dissolved in 20 ml of water and with good cooling was neutralized with saturated potash solution (to phenolphthalein). The arecoline base was extracted with benzene (3 times with 20 ml portions). The extract was dried over sodium sulfate, the benzene was distilled off, and the residue was distilled. Yield 7 g (75%).

B.p. 106-107° at 17 mm, d_4^{20} 1.0496, n_D^{20} 1.4790, MR_D 41.92. $C_8H_{13}O_2N$. Calculated MR_D 42.07.

b) From N-Methyl-4-hydroxyhexahydronicotinic Acid Hydrochloride (X, R = $CH_3 \cdot HCl$). To 21.7 g of technical N-methyl-4-hydroxyhexahydronicotinic acid hydrochloride was added 65 g of thionyl chloride. The mixture was heated at the boil for 3 hours, then the excess thionyl chloride was removed by vacuum-distillation, and the residue was treated with 65 ml of anhydrous methyl alcohol to convert the formed acid chloride (XI, R = = $CH_3 \cdot HCl$) to the methyl ester. After standing at room temperature for 2 hours and heating at the boil for 1 hours the excess alcohol was removed by vacuum-distillation. The residue was dissolved in 100 ml of water. Further treatment was the same as described for the isolation of the arecoline base after the dehydration of N--methyl-3-carbomethoxy-4-hydroxypiperidine. Yield 10.3 g (61.2%). B.p. 110-112% at 20 mm. The yield of the arecoline base was reduced by 5-10% when either phosphorus trichloride or phosphorus oxychloride was used a as the dehydrating agent.

The bases of the arecoline homologs: ethyl (V, R = C_2H_5), n-propyl (V, R = n-C_3H_7), n-butyl (V, R = = n-C_4H_9) and benzyl (V, R = $CH_2C_6H_5$) were obtained in a similar manner by dehydration with thionyl chloride.

(V, R = C_2H_5). Yield 42.6%. B.p. 97-98° at 7 mm; d_4^{20} 1.0357, n_D^{20} 1.4835, MR_D 46.70; calc. 46.68.

Found %: C 63.88; H 9.08; N 8.26. $C_9H_{15}O_2N$. Calculated %: C 63.89; H 8.94; N 8.28.

(V, R = n-C_3H_7). Yield 48%. B.p. 115-117° at 6 mm, d_4^{20} 1.0231, n_D^{20} 1.4850, MR_D 51.33; calc. 51.31.

Found %: C 65.78; H 9.46; N 7.61. $C_{10}H_{17}O_2N$. Calculated %: C 65.52; H 9.35; N 7.64.

(V, R = n-C_4H_9). Yield 40.8%. B.p. 116-117° at 5 mm, d_4^{20} 1.0141, n_D^{20} 1.4872, MR_D 55.97; calc. 55.92.

Found %: C 67.17; H 9.67; N 7.08. $C_{11}H_{19}O_2N$. Calculated %: C 66.95; H 9.73; N 7.10.

6. Arecoline Hydrobromide (VI, R = CH_3). The hydrobromides of arecoline and its homologs were isolated by the addition of a freshly prepared 35% solution of hydrogen bromide in anhydrous ethyl alcohol or of 40% hydrobromic acid to either a benzene or ether solution of the free base until acid to congo. After recrystallization from anhydrous ethyl alcohol the pure hydrobromides of arecoline and its homologs: ethyl (VI, R = C_2H_5), n-propyl (VI, R = n-C_3H_7), n-butyl (VI, R = n-C_4H_9) and benzyl (VI, R = $CH_2C_6H_5$) were obtained as either colorless needles or prisms.

(VI, R = CH_3). Yield 75-82%. B.p. 169-171°.

Found %: C 40.51; H 6.23; N 5.71. $C_9H_{15}O_2N \cdot HBr$. Calculated %: C 40.70; H 5.97; N 5.92.

The mixed melting point of the synthetic arecoline hydrobromide with the hydrobromide of the natural alkaloid (m.p. 169-170.5°) was not depressed.

(VI, R = C_2H_5). Yield 82.8%. B.p. 169-170°.

Found %: C 43.25; H 6.08; N 5.70. $C_9H_{15}O_2N \cdot HBr$. Calculated %: C 43.22; H 6.45; N 5.60.

(VI, R = n-C_3H_7). Yield 80%. B.p. 165-166°.

Found %: C 45.53; H 6.99; N 5.14. $C_{10}H_{17}O_2N \cdot HBr$. Calculated %: C 45.45; H 6.87; N 5.30.

(VI, R = n-C_4H_9). Yield 79%. B.p. 161-162°.

Found %: C 47.51; H 6.86; N 4.82. $C_{11}H_{19}O_2N \cdot HBr$. Calculated %: C 47.49; H 7.22; N 5.04.

(VI, R = $CH_2C_6H_5$). Yield 68%. B.p. 179-180°.

Found %: C 54.17; H 5.96; N 4.58. $C_{14}H_{17}O_2N \cdot HBr$. Calculated %: C 53.85; H 5.81; N 4.49.

SUMMARY

1. Starting with either methyl acrylate or with acrylonitrile, we synthesized the hydrobromide of the alkaloid arecoline.

2. A method was developed for the preparation of the homologs of arecoline: the methyl esters of N-ethyl, N-n-propyl, N-n-butyl and N-benzyl-Δ^3-tetrahydronicotinic acid.

3. The physiological testing of the synthesized compounds, made in the Moscow Veterinary Academy and in the K. I. Skryabin Institute of Helminthology (Moscow), revealed [9] that in its properties the hydrobromide of the synthetic arecoline (VI, R = CH_3) obtained by us is completely identical with the hydrobromide of the natural alkaloid. Of the homologs of arecoline only the n-propyl member (VI, R = n-C_3H_7) shows slight general physiological activity.

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STUDY OF ALKALOIDS FROM CAREX BREVICOLLIS D. C.

I. V. Terentyeva and G. V. Lazuryevsky

Of the numerous varieties of sedge grasses, most of them forage plants, the Parva sedge grass (Carex brevicollis D.C.) is characterized by being poisonous and is not eaten by animals. Locally the properties of this plant are known, and consequently in many regions the Parva sedge grass is called "loco grass." This plant grows widespread in the light forest areas of Moldavia, and is found in Caucasia and along the shore of the Black Sea [1]. Plants of the genus Carex have not been subjected to detailed chemical study and up to now have not been classified as belonging to the alkaloid-bearing plants. In addition, it was decided by V. S. Sokolov [2] that the whole family of sedge grasses is "lacking in promise" in this respect.

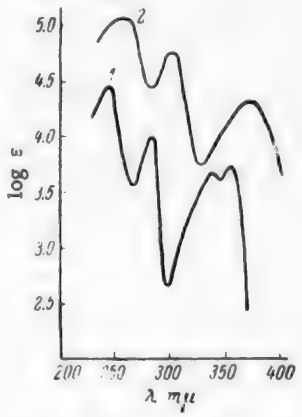

Fig. 1. Absorption curves of brevicolline and its dihydrochloride in the ultraviolet region of the spectrum.
1) Brevicolline, $c = 1.185 \cdot 10^{-4}$ M,
2) brevicolline dihydrochloride, $c = 0.44 \cdot 10^{-4}$ M.
The data were recalculated to the corresponding length of the layer.

It was established by us that alkaloids are present in some varieties of sedge grasses (C. brevicollis D. C., C. Michelli Host, C. pilosa Scop), and that they are new compounds [3], not reported before in the literature. The present paper is devoted to a study of the Parva sedge grass. The total alkaloid bases in C. brevicollis D. C. were isolated either by extraction with dichloroethane or by treatment of the plant matter with dilute sulfuric acid solution to give the alkaloids as a brownish powder, difficultly soluble in water. The total amount of alkaloids was 0.5% (based on air dried material).

The chief alkaloid, which we named brevicolline, was separated from the other bases present by recrystallization from methanol, and then was purified through the hydrochloride. Brevicolline is a white crystalline compound with m.p. 223-224°, and is optically active. Its composition was determined to be $C_{17}H_{19}N_3$. Brevicolline gives a number of well-defined crystalline salts and derivatives.

The UV spectra of an alcohol solution of brevicolline have four maxima. The character of the absorption curves (Fig. 1, Curve 1) enables us to classify the alkaloid as belonging to the class of complex indole compounds [4]. A water solution of brevicolline dihydrochloride shows three absorption maxima. The general shape of the curve (Fig. 1, Curve 2) is similar to that of the absorption curve for the free base, although in the former case a slight shift in the visible region of the spectrum is observed, and also some increase in the intensity of absorption.

The IR spectra are shown in Fig. 2. They indicate the absence of oxygen-containing functions in the brevicolline molecule and the presence of double bonds and of the >NH and $>NCH_3$ groups.

Potentiometric titration, using a glass electrode, of alcohol solutions of brevicolline with 0.1 N HCl gives 2 ill-defined jumps; however, the titration curve clearly shows that the alkaloid is dibasic (Fig. 3). The third nitrogen atom, present in the brevicolline molecule, is apparently without basic properties.

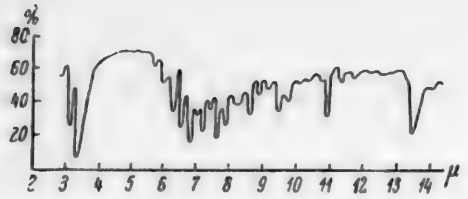

Fig. 2. Absorption of brevicolline in the infrared region of the spectrum.

Brevicolline gives a number of color reactions, characteristic for alkaloids of the indole series. Solutions of salts of the base show an intense sky-blue fluorescence. By the paper chromatographing of the methanolic mother liquors, obtained after the major portion of the brevicolline had been removed, it was shown that at least three other alkaloids are present (I – III, cf. Table).

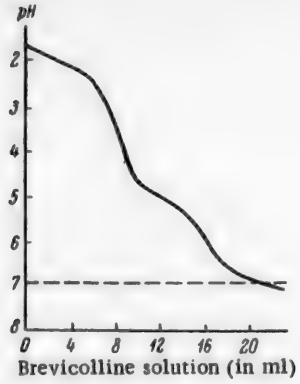

Fig. 3. Potentiometric titration of brevicolline.

EXPERIMENTAL*

Isolation of Brevicolline. The alkaloids were extracted with dichloroethane in the usual manner. From 2 kg of plant matter we obtained 10 g (0.5%) of total alkaloid bases. Recrystallization from methanol and purification through the hydrochloride gave 6.4 g of brevicolline as the free base (64% of the sum). M.p. 223-224°. $[\alpha]_D^{20}$ −145.8 (*I* 1.9009, c 1.8087 in alcohol).

Found %: C 76.93, 77.18; H 7.26, 7.33; N 15.54, 15.85; NH 7.48, 6.05; NCH_3 11.30, 10.24. $C_{17}H_{19}N_3$. Calculated %: C 76.93; H 7.22; N 15.84; NH 5.66; NCH_3 10.94.

Brevicolline Dihydrochloride was obtained from a saturated alcohol solution of the free base by precipitation with concentrated hydrochloric acid. White crystalline compound, m.p. 273° (from methanol).

Found %: C 58.27, 58.53; H 6.42, 6.51; N 12.32, 12.18; Cl 20.23, 20.25. $C_{17}H_{19}N_3 \cdot 2HCl \cdot 0.5H_2O$. Calculated %: C 58.78; H 6.39; N 12.11; Cl 20.42.

Brevicolline Dihydriodide deposited as a yellow powder when a saturated alcohol solution of brevicolline was acidified with concentrated hydriodic acid. M.p. 252-253° (from methanol).

Found %: I 48.61, 48.51. $C_{17}H_{19}N_3 \cdot 2HI$. Calculated %: I 48.70.

Brevicolline Methiodide. To 1 g of brevicolline, dissolved in 40 ml of acetone, was added 1 ml of methyl iodide. Crystals of the methiodide deposited after the mixture had stood for 15-20 minutes. Recrystallization from a mixture of methanol and water (3 : 1) gave filamentous yellow crystals with m.p. 210-212°.

Found %: I 31.35. $C_{18}H_{22}N_3I$. Calculated %: I 31.12.

The addition of 10% sodium hydroxide solution to a water solution of brevicolline methiodide gave a copious precipitate of methylbrevicolline. Yellow-green crystals from aqueous methanol. M.p. 189-191°.

Methylbrevicolline Methiodide. A solution of 1 g of methylbrevicolline in 30 ml of acetone was treated with 1 ml of methyl iodide. The solution was allowed to stand for 1-2 hours. The deposited methylbrevicolline was recrystallized from water. M.p. 247-248°. It failed to undergo cleavage under the conditions of the Hofmann reaction, and gave back the starting methylbrevicolline.

Found %: I 30.46. $C_{18}H_2N_3 \cdot CH_3I$. Calculated %: I 30.14.

Brevicolline Dimethiodide. A mixture of 1 g of brevicolline and 9 ml of methyl iodide was heated in an autoclave at 120° for 2 hours. We obtained 1.8 g (94.7%) of the dimethiodide. M.p. 263-264° (from C_2H_5OH + + H_2O 2 : 1).

*P. Vember and A. Borovkov participitated in the work.

Found %: I 46.82. $C_{17}H_{19}N_3 \cdot 2CH_3I$. Calculated %: I 46.47.

An SF-4 spectrophotometer was used to take the UV spectra. For alcohol solutions of brevicolline at a concentration of $1.135 \cdot 10^{-4}$ M we obtained λ_{max} 245 mμ (log ε 4.42), 288 mμ (log ε 3.98), 338 mμ (log ε 3.64), 352 mμ (log ε 3.69). For a water solution of brevicolline dihydrochloride at a concentration of $0.44 \cdot 10^{-4}$ M we obtained λ_{max} 262 mμ (log ε 4.6), 306 mμ (log ε 4.3), 372.5 mμ (log ε 3.9).

The Potentiometric Titration was run with a glass electrode. When 0.7770 g of brevicolline in 100 ml of alcohol was titrated with 5 ml of 0.1 N hydrochloric acid solution the first jump came at 8.25 ml of the free base solution, equiv. wt. 129.5; the second jump came at 16.0 ml.

Found: M 250. $C_{17}H_{19}N_3$. Calculated: M 265.4.

Color Reactions of Brevicolline. With concd. H_2SO_4 – a pink color changing to a violet; with concd. HNO_3 – a yellow color; with Marki* reagent (sulfuric acid + formaldehyde) – a green color; with p-dimethylaminobenzaldehyde in sulfuric acid – a red color.

Chromatography. The method of ascending paper chromatography was used (paper No. 4). The solvents were: 1) n-butyl alcohol, acetic acid and water in the ratio 4 : 1.2 : 2.4; 2) the same solvent mixture in the ratio 25 : 1 : 25; 3) isoamyl alcohol, acetic acid and water in the ratio 25 : 1 : 25; and 4) ethyl acetate, formic acid and water in the ratio 10 : 1 : 3. The developer was Dragendorff reagent. The time of chromatographing was 20 hours. The moving front of the solvent was 25-30 cm.

Solvents	Above ground portion of the plant			
	alkaloid I R_f	alkaloid II R_f	brevicolline R_f	alkaloid III R_f
1	0.76	0.63	0.54	–
2	–	0.52	0.28	–
3	–	0.33	0.10	–
4	0.69	0.25	–	–
	Roots of the Plant			
1	0.78	0.68	0.58	0.40

SUMMARY

1. The presence of alkaloid-bearing plants in the family of sedge grasses was shown for the first time.

2. A new alkaloid, having the composition $C_{17}H_{19}N_3$, was isolated from Carex brevicollis, D. C., and partially characterized.

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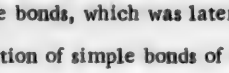
A DISCUSSION

THE PROBLEM OF σσ -CONJUGATION

V. I. Minkin

In 1935 Baker and Nathan [1] introduced the concept of hyperconjugation – the conjugation of simple and multiple bonds, which was later explained on a physical basis [2]. They also postulated that it is possible to have conjugation of simple bonds of the type  , where X can exist as an anion.

The basic investigations on the problem of the conjugation of simple bonds (σσ -conjugation) have been made by Soviet scientists [3], who studied this effect mainly on the example of organometallic compounds. However, the conjugation of simple bonds can also be shown quite clearly in the chemical behavior of nonmetalloorganic compounds, as was shown on the example of some reactions of alkyl chlorocarbonates [4].

The present comments are a further attempt to explain the reactivity of certain compounds from the viewpoint of σσ -conjugation. In particular, we discuss the problem of the different influence exerted by such substituents as the methyl and ethyl groups on the chemical behavior of phenol ethers and of alkylanilines.

It had been mentioned earlier [5] that an ethoxyl group in aromatic compounds exerts a stronger ortho–para orienting influence than does the methoxyl group, which was associated by the authors of the cited work [5] with the greater polarizability shown by the ethyl radical. The ethylamine group is also apparently more nucleophilic than the methylamine group. This is confirmed by the following examples.

The velocity constant for the chlorination of p-chlorophenetole is higher than for the chlorination of p-chloroanisole [6]. In such typical electrophilic substitutions as the synthesis of ketones by the Gustavson–Friedel–Crafts and Hoesch methods, under similar experimental conditions, the ethoxy ketones are obtained in better yield than are the methoxy ketones. This is also true in the case of propionylation [7, 8], and in the formation of 4-alkoxybenzoylpropionic acids when anisole [9], phenetole [10] and the methyl [11] and ethyl [12] ethers of o-cresol are acylated with succinic anhydride. In a similar manner phenetole [13], reacted by the Hoesch method with trichloromethyl cyanide, gives a higher yield of the 4-alkoxy-ω-trichloroacetophenone than when anisole is used [13], while the reaction of m-chlorophenetole with hydrogen cyanide gives a better yield of the corresponding 2-chloro-4-alkoxybenzaldehyde than when anisole is used [14]. The p-ethoxy- and p-ethylaminobenzoic acids are weaker than the corresponding p-methoxy- and p-methylaminobenzoic acids.

The results of measuring the dipole moments [15, 16] of aliphatic compounds, and also of phenol ethers and substituted anilines, which prove to be nearly equivalent for corresponding pairs of compounds, reveal that such differences in the orienting influence cannot be regarded as being entirely due to the greater static inductive effect of the ethyl radical.

Since the difference in the influence of the discussed substituents also appears in chemical reactions, then it must be regarded as being due to a dynamic effect. This is confirmed by calculating the exaltations of the molecular refraction.*

The data given in the Table reveal that the EM_D values for the ethyl derivatives are always higher than the EM_D values for the methyl derivatives. From the very selection of compounds discussed it follows that such

* In calculating the molecular refractions we used the bond refraction values given in [17].

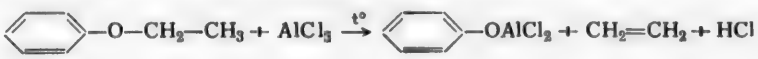
additional increase in the exaltation of the molecular refraction can be regarded only as being due to some sort of dynamic effect exerted by the ethyl radical. In our opinion, σσ-conjugation can be such an effect, which is in accord with the concepts [3] that the conjugation of simple bonds is a dynamic effect.

Comparison of the Molecular Refraction Exaltation Values for the Ethyl and Methyl Derivatives of Some Organic Compounds

Compound	MR_D		Exaltation EM_D
	calculated	found	
$C_6H_5NHC_2H_5$	39.08	40.41	1.33
$C_6H_5NHCH_3$	34.44	35.61	1.17
$C_6H_5OC_2H_5$	37.26	37.61	0.35
$C_6H_5OCH_3$	32.62	32.86	0.24
$C_6H_5SC_2H_5$	43.40	44.07	0.67
$C_6H_5SCH_3$	38.76	39.36	0.60
o-$NO_2C_6H_4OC_2H_5$	42.94	44.29	1.35
o-$NO_2C_6H_4OCH_3$	38.30	39.58	1.28
$C_6H_5N(C_2H_5)_2$	48.56	50.24	1.68
$C_6H_5N(CH_3)_2$	39.27	40.81	1.54

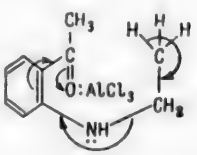
Actually, the oxygen in phenol ethers and the nitrogen in amines is found in pπ-conjugation with the benzene ring, and on the strength of this can serve as acceptors of electrons from the ethyl radical linked with them, while the $C_6H_5O^-$ and $C_6H_5NH^-$ groups exist as anions. It is obvious that this effect is not manifested in the corresponding aliphatic compounds, for in the latter case an acceptor of electrons, like the phenyl radical, is absent.

To be sure, the σσ-conjugation effect in such compounds is expressed to a weaker degree than is true for organometallic compounds, but nevertheless the semblance of a double bond, appearing between the second and third atoms of the conjugated chain, shows up in the addition of a strongly electrophilic agent. Such a case is the dealkylation of phenetole with aluminum chloride at high temperatures.



With the proposed theory it is also easy to explain the greater lability of the bond between the ethyl radical and either oxygen or nitrogen, when compared to the methyl radical. This appears, for example, in the greater ease with which phenetole suffers alkaline hydrolysis [18], or in the greater ease with which salts of ethylaniline undergo the Hofmann rearrangement, when compared with the salts of methylaniline [19].

The σσ-conjugation effect also appears in other reactions of such compounds. Thus, we recently studied [20] the rearrangement of N-ethylacetanilide in the presence of aluminum chloride and found that the reaction proceeds through the stage of the intermediate formation of o-ethylaminoacetophenone by the mechanism of σσ--conjugation, consisting in the polarization of the carbonyl group during complex formation with aluminum chloride, which leads to cyclization not at the methylene group, which gives quinaldine in the final analysis [21], but at the methyl group with the formation of lepidine.



We will mention that the greater activity shown by the hydrogens on the β-carbon atom of a side chain cannot be explained by the theory of inductive polarizability.

The fact that lepidine, and not quinaldine, is formed in our studied acetylation of N-ethylacetanilide by the Gustavson–Friedel–Crafts method is also explained in a similar manner.

What has been said above with respect to the ethyl radical can also be used to explain the influence exerted

by the higher alkyl radicals in substituted phenols and anilines when compared with the methyl radical.

It is necessary to mention that the theory proposed by us cannot be strictly argued due to the absence as yet of any physical theory of the conjugation of simple bonds, however it does make it possible to satisfactorily explain some of the peculiarities of the influence exerted by the higher alkyls on the reactivity of phenol ethers and aliphatic aromatic amines.

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* Russian translation.
** In Russian.
*** Original Russian pagination. See C. B. translation.

LETTER TO THE EDITOR

In reply to my letter, published in your journal,* B. M. Mikhailov and I. K. Platova** acknowledge that they failed to cite my work on the synthesis of amines of the thiazole series for the reason that they were not familiar with it. However, in their reply they place in doubt the 4-methyl-2-dimethylaminoethylthiazole synthesized by myself, being motivated by the difference in the melting points of the picrates and methiodides of this base, and also by the absence in my paper of the analysis of the picrate for carbon and hydrogen (the picrate was analyzed for nitrogen).

To this criticism I reply as follows.

1. The preparation of amines of the thiazole, benzothiazole and α-naphthothiazole series was run by me under the typical conditions of the Mannich reaction, and specifically by heating an ethanol solution of the corresponding thiazole base with paraformaldehyde and dimethylamine hydrochloride for many hours.*** For this reason it seems strange for B. M. Makhailov and I. K. Platova to state that the Mannich reaction with 2,4-dimethylthiazole can proceed only in the presence of hydrochloric acid. According to the indicated authors, it was only under these conditions that they were able to obtain the two bases: 4-methyl-2-β-dimethylaminoethylthiazole (picrate, m.p. 105-106.5°) and 4-methyl-2-di(dimethylaminomethyl)methylthiazole (methiodide, m.p. 208-209°).

2. The 4-methyl-2-dimethylaminoethylthiazole picrate that I obtained had m.p. 157-168° and is the dipicrate with composition $C_{20}H_{20}O_{14}N_8S$, which was confirmed by analysis for nitrogen and by the additional determination of sulfur (incidentally, there was no need to analyze the picrate for carbon and hydrogen). The analysis results were as follows:

Found %: N 17.87; S 5.02, 4.97. $C_{20}H_{20}O_{14}N_8S$. Calculated %: N 17.82; S 5.09.

The methylation of this base gave the diquaternary salt with composition $C_{10}H_{20}N_2SI_2$, and having m.p. 196-197°, the structural formula of which is given in the text of my paper. Additional analysis of the compound for iodine supports this structure.

In addition, the boiling point of 4-methyl-2-dimethylaminoethylthiazole at atmospheric pressure is given in my paper, and also the styphnate and perchlorate of this base were prepared.

B. M. Mikhailov and I. K. Platova compare compounds that cannot be compared; for example, the melting point of the diquaternary salt of 4-methyl-2-dimethylaminoethylthiazole (obtained by me) with that of the diquaternary salt of 4-methyl-2-di(dimethylaminomethyl)-methylthiazole (obtained by them), and also a comparison of the picrate with the dipicrate of this base. On the bases of such incorrect comparison they conclude that the base obtained by me from 2,4-dimethylthiazole by the Mannich reaction is not 4-methyl-2-dimethylaminoethylthiazole.

Before putting any experimental data in doubt, it is customary practice to first check them and then make the proper conclusions.

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L. Mushkalo

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** J. Gen. Chem. 27, 833 (1957). (Original Russian pagination. See C. B. translation).
*** Ukrain. Chem. J. 15, 467 (1949).

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* Due to an error in pagination which was discovered too late to remedy, there is a ten-page jump between the last page of the previous article and the first page of this article.

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